

AB

**LIGNOCELLULOSE COMPOSITION COMPRISING LIGNOPHENOL DERIVATIVE
AND CELLULOSE COMPONENT****Publication number:** JP2001342353**Publication date:** 2001-12-14**Inventor:** FUNAOKA MASAMITSU; MORITA SHUJI**Applicant:** FUNAOKA MASAMITSU**Classification:****- International:** C08B1/00; C08J5/00; C08L1/00; C08L97/02;
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C08L97/02; C08B1/00; C08J5/00; C08L1/00**- European:****Application number:** JP20010066429 20010309**Priority number(s):** JP20010066429 20010309; JP20000096221 20000331**Report a data error here****Abstract of JP2001342353**

PROBLEM TO BE SOLVED: To provide a means to convert a wood resource having fixed material characteristics into a novel moldable resource, such as a plastic. **SOLUTION:** A lignocellulose composition comprising a lignophenol derivative and a cellulose component is obtained by adding an acid to a phenol derivative- supplemented lignocellulose substance and mixing these.

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(54) 【発明の名称】 リグノフェノール誘導体とセルロース成分とから成るリグノセルロース系組成物

(57) 【要約】

【課題】 材料特性が固定された木質資源をプラスチックのように成型加工が可能な新しい機能性資源へと転換利用する手段を提供すること。

【解決手段】 フェノール誘導体を添加したリグノセルロース系物質に酸を添加して混合することにより得られる、リグノフェノール誘導体とセルロース成分とから成るリグノセルロース系組成物。

【特許請求の範囲】

【請求項1】 フェノール誘導体を添加したリグノセルロース系物質に酸を添加して混合することにより得られる、リグノフェノール誘導体とセルロース成分とから成るリグノセルロース系組成物。

【請求項2】 リグノフェノール誘導体成分とセルロース成分とが均一系を形成している、請求項1に記載のリグノセルロース系組成物。

【請求項3】 酸として、セルロースを膨潤させる作用を有し、かつセルロースを加水分解する作用が低い酸を使用する、請求項1又は2に記載のリグノセルロース系組成物。

【請求項4】 酸が、リン酸、ギ酸又はトリフルオロ酢酸である、請求項1から3の何れかに記載のリグノセルロース系組成物。

【請求項5】 リグノセルロース系物質に添加するフェノール誘導体が、オルト位及び／又はパラ位に1以上の置換基を有しているフェノール誘導体である、請求項1から4の何れかに記載のリグノセルロース系組成物。

【請求項6】 リグノセルロース系物質に添加するフェノール誘導体が、低級アルキル基、低級アルコキシ基又は水酸基から選択される1以上の置換基をオルト位及び／又はパラ位に有しているフェノール誘導体である、請求項1から5の何れかに記載のリグノセルロース系組成物。

【請求項7】 p-クレゾール、2,6-キシレノール、2,4-キシレノール、2-メトキシフェノール(Guaiacol)、2,6-ジメトキシフェノール、カテコール、レゾルシノール、ホモカテコール、ピロガロール及びフロログルシノールから成る群から選ばれるフェノール誘導体を添加したリグノセルロース系物質に95%リン酸を添加して混合することにより得られる、リグノフェノール誘導体とセルロース成分とから成るリグノセルロース系組成物。

【請求項8】 リグノフェノール誘導体がアシル化又はメチロール化されている、請求項1から7の何れか1項に記載のリグノセルロース系組成物。

【請求項9】 可塑化材料であることを特徴とする、請求項1から8の何れか1項に記載のリグノセルロース系組成物。

【請求項10】 請求項1から9の何れか1項に記載のリグノセルロース系組成物から成る成形体。

【請求項11】 リグノセルロース系物質をフェノール誘導体で処理することによりリグニン成分を該フェノール誘導体で溶媒和して得られる混合物に酸を添加して混合する工程を含む、請求項1から9の何れか1項に記載のリグノセルロース系組成物の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、リグノフェノール

誘導体とセルロース成分とからなるリグノセルロース系組成物に関する。より詳細には、本発明は、木材などのリグノセルロース系物質にフェノール誘導体を着着させた後に酸で処理することによって得られるリグノフェノール誘導体とセルロース成分とから成るリグノセルロース系組成物に関する。

【0002】

【従来の技術】現代社会においては化石資源の利用は不可欠なものとなっているが、化石資源は再生産が不可能であり、近い将来枯渇が懸念されている。化石資源に替わる資源の一つとしてバイオマス資源が着目されている。バイオマス資源の中でも木質系バイオマスは、地球上に膨大に存在し、短期間で生産可能であり、適切な維持管理により持続的な供給が可能な資源である点、さらに資源としての利用後は、自然界で分解し、新たなバイオマス資源として生まれ変わるという点で着目されている。

【0003】木質系バイオマス資源、即ち、リグノセルロース系資源は、セルロースやヘミセルロース等の親水性炭水化合物と疎水性のリグニン（ポリフェノール）とから構成され、これらは細胞壁中で相互侵入高分子網目（IPN）構造をとり、複雑に絡みあって複合体をなした状態で存在している。リグノセルロース系資源には、かかる複合体の構造により、各種素材としての有用性が付与されている。

【0004】リグノセルロース系資源の利用形態を考えると、第1の利用形態として、複合体のまま、所定形状の建築用材あるいは家具用材として加工して利用し、あるいは、木質チップやファイバー等の成形用材料等として利用する直接的な利用形態があり、第2の利用形態として、複合体の構成成分であるセルロースを抽出してパルプ化する間接的な利用形態とがある。ここに、今後の化石資源の枯渇を考慮して森林資源の有効利用を考えた場合、これらの双方の利用形態において、森林資源の再利用を図ることが重要である。

【0005】しかし、現状においては、複合体たる木材をそのまま成形体として利用する直接的利用形態では、その形状や大きさのために、木材の再利用が困難であり、使用後は廃棄処分されることが多い。また、成形用素材として利用する場合には、バインダーとして熱硬化性樹脂を含有していることから、再利用が困難であった。このように、直接的利用形態においては、複合体を構成するセルロース等やリグニンについては再利用されにくいのが現状であった。

【0006】また、複合体の構成成分であるセルロースを抽出してパルプ化する間接的利用形態においては、ファイバー化とシート化とを繰り返すことにより、再生利用が図られているものの、セルロース以外の構成成分であるリグニンがほとんど利用されていない状態にある。上記のように、直接的及び間接的利用形態の何れの利用

形態においても、リグニンの再利用は図られていないのが現状である。リグニンは、地球上においてセルロースに次いで多量に存在する有機物質である。にもかかわらず、複合体たる木材中のリグニンに着目して、再利用可能な形態の木材加工体をつくり出すことやかかる木材加工体の再利用を図ることは全く考えられていない。

【0007】木質系（リグノセルロース系）バイオマス利用においてリグニンの有効な利用を図るためには、先ず木材をその構成成分に分離することが必要である。本発明者らはこれまでの研究により、濃酸による炭水化物の膨潤による組織構造の破壊と、フェノール誘導体によるリグニンの溶媒和の組み合わせにより、リグニンの不活性化を抑制し、リグノセルロース系物質をその構成成分であるリグノフェノール誘導体と炭水化物とに分離する方法を開発している（特開平2-233701号）。この方法で得られたリグノフェノール誘導体の活用法としては、例えば、セルロース系ファイバー等の成形材料に適用し成形体を作製することが報告されている（特開平9-278904号）。しかしながら、上記特許公報には、リグノセルロース系物質のうちのリグニン以外の構成成分であるセルロース成分の利用については述べられていない。

【0008】

【発明が解決しようとする課題】本発明の課題は、材料特性が固定された木質資源をプラスチックのように成型加工が可能な新しい機能性資源へと転換利用する手段を提供することである。本発明の別の課題は、リグノセルロース系物質の相分離システムを応用してセルロースの高度な会合（結晶構造）を解放すると同時に、リグニン区分をリグノフェノール状のフェノール系リニア型高分子に変換してセルロース区分と均一系を形成することである。これにより、セルロースの再結晶化が阻害されると同時にリグノフェノールの熔融温度にて総体として流動するようになり、自由成形が可能な素材が得られる。

【0009】

【課題を解決するための手段】本発明者らは上記課題を解決するために鋭意検討を重ねた結果、フェノール誘導体を添加したリグノセルロース系物質に酸を添加して混合することにより、リグノフェノール誘導体とセルロース成分とから成る均一な組成物が得られること、並びに得られる組成物が可塑性を有することを見出し、本発明を完成するに至った。

【0010】本発明によれば、フェノール誘導体を添加したリグノセルロース系物質に酸を添加して混合することにより得られる、リグノフェノール誘導体とセルロース成分とから成るリグノセルロース系組成物が提供される。好ましくは、リグノフェノール誘導体成分とセルロース成分とは均一系を形成している。好ましくは、酸として、セルロースを膨潤させる作用を有し、かつセルロースを加水分解する作用が低い酸を使用する。

【0011】好ましくは、酸は、リン酸、ギ酸又はトリフルオロ酢酸である。好ましくは、リグノセルロース系物質に添加するフェノール誘導体は、オルト位及び／又はパラ位に1以上の置換基を有しているフェノール誘導体である。

【0012】好ましくは、リグノセルロース系物質に添加するフェノール誘導体は、低級アルキル基、低級アルコキシ基又は水酸基から選択される1以上の置換基をオルト位及び／又はパラ位に有しているフェノール誘導体である。好ましくは、本発明の組成物は、p-クレゾール、2, 6-キシレノール、2, 4-キシレノール、2-メトキシフェノール（Guaiacol）、2, 6-ジメトキシフェノール、カテコール、レゾルシノール、ホモカテコール、ピロガロール及びフロログルシノールから成る群から選ばれるフェノール誘導体を添加したリグノセルロース系物質に95%リン酸を添加して混合することにより得られる、リグノフェノール誘導体とセルロース成分とから成るリグノセルロース系組成物である。好ましくは、リグノフェノール誘導体はアシル化又はメチロール化されている。好ましくは、本発明のリグノセルロース系組成物は、可塑化材料である。

【0013】本発明の別の側面によれば、上記した本発明のリグノセルロース系組成物から成る成形体が提供される。本発明のさらに別の側面によれば、リグノセルロース系物質をフェノール誘導体で処理することによりリグニン成分を該フェノール誘導体で溶媒和して得られる混合物に酸を添加して混合する工程を含む、本発明のリグノセルロース系組成物の製造方法が提供される。

【0014】

【発明の実施の形態】以下、本発明の実施方法及び実施態様について説明する。本発明のリグノセルロース系組成物は、フェノール誘導体を添加したリグノセルロース系物質に酸を添加して混合することにより得られる。リグノセルロース系物質に添加するために用いるフェノール誘導体としては、1価のフェノール誘導体、2価のフェノール誘導体、または3価のフェノール誘導体などを用いることができる。1価のフェノール誘導体の具体例としては、1以上の置換基を有していてもよいフェノール、1以上の置換基を有していてもよいナフトール、1以上の置換基を有していてもよいアントロール、1以上の置換基を有していてもよいアントロキノンオールなどが挙げられる。

【0015】2価のフェノール誘導体の具体例としては、1以上の置換基を有していてもよいカテコール、1以上の置換基を有していてもよいレゾルシノール、1以上の置換基を有していてもよいヒドロキノンなどが挙げられる。3価のフェノール誘導体の具体例としては、1以上の置換基を有していてもよいピロガロールなどが挙げられる。

【0016】1価から3価のフェノール誘導体が有して

いてもよい置換基の種類は特に限定されず、任意の置換基を有していてもよいが、好ましくは、電子吸引性の基（ハロゲン原子など）以外の基であり、例えば、低級アルキル基（メチル基、エチル基、プロピル基など）、低級アルコキシ基（メトキシ基、エトキシ基、プロポキシ基など）、アリール基（フェニル基など）、水酸基などが挙げられる。また、フェノール誘導体上のフェノール性水酸基の2つあるオルト位のうちの少なくとも片方は無置換であることが好ましい。フェノール誘導体の好ましい例としては、p-クレゾール、2, 6-キシレノール、2, 4-キシレノール、2-メトキシフェノール（Guaiacol）、2, 6-ジメトキシフェノール、カテコール、レゾルシノール、ホモカテコール、ビロガロール及びフロログルシノールなどが挙げられる。

【0017】なお、使用するフェノール誘導体の種類を選択することにより、得られる本発明のリグノセルロース系組成物の総体としての機能（親水性、疎水性、又は生理機能など）を制御することができる。また、本発明で用いるフェノール誘導体としては、4位（パラ位）に置換基を有するフェノール誘導体、及び／又は2位（オルト位）及び4位（パラ位）に置換基を有するフェノール誘導体が好ましい。4位（パラ位）に置換基を有するフェノール誘導体とは、2つのオルト位に置換基を有していないフェノール誘導体である。また、2位（オルト位）及び4位（パラ位）に置換基を有するフェノール誘導体とは、6位（片方のオルト位）に置換基を有していないフェノール誘導体である。

【0018】リグノフェノール誘導体は、アルカリ条件下で架橋性官能基形成化合物と反応させて、リグノフェノール誘導体中のフェノール性水酸基のオルト位に架橋性官能基を有する架橋性リグノフェノール誘導体を調製し、この架橋性リグノフェノールを架橋することにより高分子材料を調製して使用することもできる。この場合、使用するフェノール誘導体の種類を選択することにより、架橋性官能基の導入頻度を調節することができる。即ち、4位（パラ位）に置換基を有するフェノール誘導体を使用した場合には、該フェノール誘導体は2位又は6位の炭素原子でリグニンのフェニルプロパン単位のベンジル位の炭素原子に結合することになる。この場合、残りの2位又は6位の炭素原子の片方はフリーのまま存在し、架橋性官能基の導入部位となる。

【0019】一方、2位（オルト位）及び4位（パラ位）に置換基を有するフェノール誘導体を使用した場合には、該フェノール誘導体は6位の炭素原子でリグニンのフェニルプロパン単位のベンジル位の炭素原子に結合することになる。この場合、フリーな状態のオルト位及びパラ位は存在しないため、導入フェノール誘導体には架橋性官能基導入部位は存在しない。従って、架橋性官能基は、リグニン母体側のみに導入されることになる。このように、反応性の異なる架橋性官能基導入部位を有

するフェノール誘導体や、導入部位数がないか、あるいは異なるフェノール誘導体を1種あるいは2種以上組み合わせるリグニンを導入することにより、リグノフェノール誘導体における架橋性官能基の導入部位数を制御することができ、結果として、架橋性リグニン誘導体の架橋密度を制御することができる。

【0020】即ち、リグノセルロース系物質をフェノール誘導体の存在下で酸で処理することにより分離されるリグノフェノール誘導体又はそれを含む高分子材料において、4位（パラ位）に置換基を有するフェノール誘導体を反応性スイッチング素子として使用し、2位（オルト位）及び4位（パラ位）に置換基を有するフェノール誘導体をブロッキング性スイッチング素子として使用することにより、リグノフェノール誘導体の機能又は構造を制御することも可能である。

【0021】さらにまた、導入フェノール誘導体として2位（オルト位）及び6位（オルト位）に置換基を有するフェノール誘導体を使用した場合には、該フェノール誘導体は4位の炭素原子でリグニンのフェニルプロパン単位のベンジル位の炭素原子に結合することになる。この場合、フリーな状態のオルト位及びパラ位は存在しないため、導入フェノール誘導体には架橋性官能基導入部位は存在しない。また、2位（オルト位）及び6位（オルト位）に置換基を有するフェノール誘導体はスイッチング機能を発揮することもないため、安定なコントロール素子として機能する。本発明では、4位（パラ位）に置換基を有するフェノール誘導体、2位（オルト位）及び4位（オルト位）に置換基を有するフェノール誘導体、あるいは2位（オルト位）及び6位（オルト位）に置換基を有するフェノール誘導体を、目的に応じて適宜選択して使用することができる。

【0022】本発明で用いる「リグノセルロース系物質」とは、木質化した材料、主として木材である各種材料、例えば、木粉、チップ、廃材、端材などを挙げることができる。また用いる木材としては、針葉樹、広葉樹など任意の種類のもので使用することができる。さらに、各種草本植物、それに関連する試料、例えば、農産廃棄物なども使用できる。リグノセルロース系物質に添加する酸としては、セルロースを膨潤させる作用を有し、かつセルロースを加水分解する作用が低い酸が好ましい。酸の具体例としては、85重量%以上のリン酸、38重量%以上の塩酸、p-トルエンスルホン酸、トリフルオロ酢酸、トリクロロ酢酸、ギ酸などを挙げることができる。好ましい酸は、85重量%以上（好ましくは95重量%以上）のリン酸、トリフルオロ酢酸、又はギ酸である。

【0023】次に、本発明によるリグノセルロース系組成物の製造方法をさらに詳細に説明する。本発明のリグノセルロース系組成物はリグノフェノール誘導体とセルロース成分とを含む。本明細書で言う「リグノフェノール

ル誘導体」とは、リグニンのフェニルプロパン単位側の側鎖 α 位に、フェノール誘導体がC-C結合で導入されたジフェニルプロパン単位を含む重合体を意味するものである。この重合体における導入フェノール誘導体の量や、分子量は、原料となるリグノセルロース系材料および反応条件により変動する。

【0024】リグノセルロース系材料から本発明のリグノセルロース系組成物を得るには、かかるリグノセルロース系材料中のリグニンをフェノール誘導体で処理してリグノフェノール誘導体とする必要がある。リグノセルロース系材料中のリグニンを、リグノフェノール誘導体に変換する方法としては以下の2つの方法が挙げられる。第1の方法は、木粉等のリグノセルロース系材料に液体状のフェノール誘導体（上記で説明したもの、例えば、p-クレゾール等）を浸透させ、リグニンをフェノール誘導体により溶媒和させ、次に、リグノセルロース系材料を濃酸（上記で説明したもの、例えば、95%リン酸）を添加し混合して、セルロース成分を溶解する。この方法によると、リグニンを溶媒和したフェノール誘導体と、セルロース成分を溶解した濃酸とが2相分離系を形成する。フェノール誘導体により溶媒和されたリグニンは、フェノール誘導体相が濃酸相と接触する界面においてのみ、酸と接触され、酸との接触により生じたリグニン基本構成単位の高反応サイトである側鎖 α 位（ベンジル位）のカチオンが、フェノール誘導体により攻撃される。その結果、前記 α 位にフェノール誘導体がC-C結合で導入され、またベンジルアリアルエーテル結合が解裂することにより低分子化される。これによりリグニンが低分子化され、同時にその基本構成単位のベンジル位にフェノール誘導体が導入されたリグノフェノール誘導体がフェノール誘導体相に生成される。

【0025】第2の方法は、リグノセルロース系材料に、固体状あるいは液体状のフェノール誘導体を溶解した溶媒（例えば、エタノールあるいはアセトン）を浸透させた後、溶媒を留去する（フェノール誘導体の収着工程）。次に、このリグノセルロース系材料に濃酸（上記で説明したもの、例えば、95%リン酸）を添加してセルロース成分を溶解する。この結果、第1の方法と同様、フェノール誘導体により溶媒和されたリグニンは、濃酸と接触して生じたリグニンの高反応サイト（側鎖 α 位）のカチオンがフェノール誘導体により攻撃されて、フェノール誘導体が導入される。また、ベンジルアリアルエーテル結合が解裂してリグニンが低分子化される。

【0026】上記反応混合物から本発明のリグノセルロース系組成物を調製するためには、濃酸処理後の全反応液を過剰の水中に投入し、不溶区分を遠心分離にて集め、脱酸後、乾燥すればよい。この乾燥物の中には、リグノフェノール誘導体とセルロース成分が均一に存在している。本発明のリグノセルロース系組成物は通常流動性を有するものである。しかし、該組成物中のリグノフ

ェノール区分を抽出すると流動性は失われる。従って、本発明のリグノセルロース系組成物ではリグノフェノール区分が重要な可塑効果を発現しているものと考えられる。

【0027】また、本発明のリグノセルロース系組成物中におけるリグノフェノール誘導体をアシル化（例えば、アセチル化など）することにより、該組成物の流動性を高めることができる。即ち、本発明のリグノセルロース系組成物中においてリグノフェノール誘導体はそれ同士、あるいはセルロース区分と水素結合で結合し、素材同士が会合する傾向がある。この場合、該組成物に流動性はそれ程高くはない。しかし、リグノフェノール誘導体をアシル化（例えば、アセチル化など）することにより素材間の会合を解消することができ、これによりリグノセルロース系組成物全体の流動性が向上し、成形体などへの加工の際の加工エネルギーを低下させることができる。さらに、本発明のリグノセルロース系組成物中におけるリグノフェノール誘導体はメチロール化して用いてもよい。メチロール化した材料を用いた場合、比較的密度が低く、吸水率が高く、しかも優れた安定性を有する成形物を作製することができる。

【0028】本発明のリグノセルロース系組成物は、任意の形態に加工することができ、好ましくは成形体に成形して使用したり、樹脂材料として木材製品の修復剤として使用することができる。例えば、本発明のリグノセルロース系組成物は、型を使用したり、ダイを通過させることなどによって所望の形状に成形して、成形品を作製することもできる。成形方法としては、例えば、射出成形、圧縮成形、繊維またはフィルムの押出、材の押出、ガス流紡糸、粘着紡糸、支持体被覆などが挙げられる。

【0029】本発明のリグノセルロース系組成物を用いて成形体を製造するに際しては、用いる材料の種類によって、成形前の仮成形工程、あるいは成形方法を各種選択し、付加し、さらに、他の追加的工程も付加することができる。あるいは、本発明のリグノセルロース系組成物は、メルト、粒子、あるいは揮発性溶媒中の溶液などの任意の形態で使用する事ができる。

【0030】本発明のリグノセルロース系組成物の用途は特に限定されないが、成形品の例としては、包装用のフィルム、被覆製品（紙、厚紙及び不織布など）、繊維、不織布、押出成形ネット、身体衛生用品、瓶および飲用容器、農業用および園芸用フィルムおよび容器、徐放装置などが挙げられる。あるいはまた、本発明のリグノセルロース系組成物は樹脂材料として、例えば木工製品の修復剤として使用することも可能である。

【0031】本発明のリグノセルロース系組成物からリグノフェノール誘導体を抽出・分離するには単純な溶媒浸漬のみで行うことができる。具体的には、本発明のリグノセルロース系組成物をリグノフェノール誘導体親和

性溶媒（例えば、アセトン等）に浸漬し、あるいは、浸漬に加えて攪拌する。溶媒可溶画分を回収することによりリグノフェノール誘導体を容易に回収することができる。このように、本発明のリグノセルロース系組成物は、その構成成分の分離及び再利用が容易であり、資源循環を効果的に達成することができる。

【0032】本発明のリグノセルロース系組成物から成形した製品についても本発明のリグノセルロース系組成物からのリグノフェノール誘導体の回収と同様に、製品の使用後、リグノフェノール誘導体を容易に回収することができる。リグノフェノール誘導体の回収は、具体的には以下の通り行うことができる。即ち、成形体の原型を維持した状態、あるいは小片に加工した状態で、リグノフェノール誘導体親和性溶媒に浸漬し、あるいは、浸漬に加えて攪拌する。この結果、リグノフェノール誘導体は、溶媒中に溶出される。成形体を小片とするとともに、溶媒中で攪拌することにより、迅速な分離抽出が可能となる。また、成形体原型を維持したい場合には、リグノフェノール誘導体親和性溶媒でも非水系の溶媒（例えばアセトン）に浸漬して、攪拌することなく放置して抽出する。このようにして回収されるリグノフェノール誘導体は、再度、成形体の製造をはじめ各種分野において利用することができる。また、同時に分離されたセルロース系材料も、再度、成形体の製造をはじめとする各種加工品に利用することができる。本出願が主張する優先権主張の基礎となる日本特許出願である特願2000-962221に記載の内容は全て開示として本明細書中に引用される。

【0033】

【実施例】実施例1：リグノセルロース系組成物の調製と評価

(1) 予備実験

(1-1) 脱脂試料の調製

ヒノキ (*Chamaecyparis obtusa*) 及びブナ (*Fagus crenata*) の木粉を振動ミル (HEIKO製作所 T I-50) にて微粉化し、80 mesh のふるい (IIDA製作所) にかかけ、80 mesh pass の木粉を得た。この木粉をエタノール：ベンゼン=1：2で48時間抽出後、ドラフト内で溶媒を完全に留去し、供試試料とした。

(1-2) 脱脂試料の含水率の測定

脱脂試料を恒量既知の秤量瓶に1g精秤し、送風乾燥機 (105℃) にて絶乾木粉重量を測定し、乾燥前の気乾木粉重量との差から含水率を求め、補正計算に用いた。

【0034】(1-3) 脱脂試料のリグニン量測定 (クラソン法)

脱脂試料を100ml容ビーカーに1g精秤し、20℃の7.2%硫酸15mLを少量ずつガラス棒で練り込みながら加え、20℃の水浴中で反応が均一に進行するように十分に攪拌しながら4時間20℃で反応させた。反応後、予め575mlに印をした1000ml容三角フラ

スコに定量的に移し、脱イオン水を加えて、硫酸濃度を3%まで希釈した。希釈した処理物を加熱し、硫酸濃度を3%に保つため、リービッヒ冷却器を使わずに時々脱イオン水を加えながら2時間煮沸した。処理後、恒量既知の1G4ガラスフィルターを用いて内容物を濾過し、不溶解物を熱水で洗浄後、105℃で乾燥させ、恒量を測定した (酸不溶性リグニン)。濾液は広葉樹の場合、3%硫酸にて10倍に希釈した後、JASCO UV-520にて205nmでの吸光度を測定し、酸可溶性リグニン量を求めた。

【0035】<酸可溶性リグニン計算方法>

$$B = A / (110 \times D)$$

$$\text{リグニン}(\%) = (B \times V \times 100) / (1000 \times W)$$

D：希釈率、W：試料重量、V：全ろ液量、A：吸光度

【0036】(2) リン酸系相分離処理

(2-1) フェノール誘導体の収着

500ml容ビーカーに脱脂木粉23gを取り、各種フェノール誘導体 (p-クレゾール、2, 6-キシレノール、2, 4-キシレノール、2-メトキシフェノール (Guaiacol)、2, 6-ジメトキシフェノール、カテコール、レゾルシノール、ホモカテコール、ピロガロール及びフロログルシノール) のアセトン溶液 (リグニンC9単位当たり3モル倍のフェノール誘導体を含む) を加え、ガラス棒で攪拌し、アルミホイルおよびパラフィルムでビーカーに蓋をし、24時間静置させた。その後、ドラフト内で木粉を激しく攪拌し、アセトンを留去した。

(2-2) リン酸処理 (相分離処理)

フェノール誘導体収着木粉に9.5%リン酸200ml (50℃) を3回に分けて加え、ガラス棒およびテフロン (登録商標) へらで練り込み、1時間50℃で激しく攪拌した。その後、反応物を約3500mlの脱イオン水に投入することでリン酸濃度を10%以下にし、反応を停止させ、さらに反応物を分散させるためにスターラーで1時間激しく攪拌した。次に、遠心分離 (8800rpm、8分、4℃) により不溶画分を回収し、脱酸を行い、凍結乾燥・減圧乾燥し、相分離処理木粉を得た。こうして得られた試料はリグノフェノール誘導体とセルロース成分と均一に含む組成物 (本明細書では、リグノセルロース系組成物とも称する) である。

【0038】(2-3) リン酸系相分離処理木粉の分画以下、2-2で得られたリグノフェノール誘導体とセルロース成分と均一に含む組成物中におけるリグノフェノール誘導体の特徴を調べることを目的として、リグノフェノール誘導体をセルロース成分から分離した。まず、(2-2) のリン酸処理で得られた相分離処理木粉8~10gを300ml容三角フラスコにとり、アセトン200mlを加え、密栓し、スターラーにて24時間激しく攪拌した。その後、遠心分離 (3500rpm、5

分、5℃)、濾過(Whatman GF/A)により分画した。不溶画分には同様の操作を行い、2回目のアセトン抽出を行った。溶媒留去後、五酸化ニリン上で減圧乾燥した。可溶画分はロータリーエバポレーターにて20mlまで濃縮後、激しく攪拌された大過剰のジエチルエーテル(500ml容三角フラスコにジエチルエーテル400ml)に滴下し、綿状の沈殿区分を遠心分離(3500rpm、5分、5℃)にて回収、ジエチルエーテルで3回洗浄し、溶媒留去後、五酸化ニリン上で減圧乾燥を行った。

【0039】(2-4) アセチル化処理

リグニン試料(アセトン可溶-エーテル不溶画分)100mgを5mlのバイアルに取り、ピリジン1mlを加え、リグニン試料を完全に溶解させた後、無水酢酸1mlを加え、室温にて48時間放置した。その後、反応物を40mlの冷水に滴下し、不溶画分を遠心分離(3500rpm、10分、5℃)にて回収し、冷水で洗浄した後、凍結乾燥・減圧乾燥させた。

【0040】(3) 素材の物性試験・構造解析

(3-1) 熱機械分析(TMA)

熱機械分析では変換素材の相転移点および軟化速度を測定した。試料をアルミバンに入れ、鉛直下向きに荷重をかけ、一定の昇温速度で所定温度まで熱を加え、そのときどきの試料の変位量をプロットした。測定は、Thermo Plus TMA (8310)(理学電気株式会社製)を用いて以下の条件で行った。

試料重量: 5mg

アルミバン: 5mm径×2.5mm

TMA荷重: 5.00g

昇温速度: 2℃/分

終了温度: 250℃

【0041】(3-2) リグノフェノール誘導体のゲル濾過クロマトグラフィー(GPC)による分子量の測定
安定剤および不純物を除去するために、精留・脱気したテトラヒドロフラン(THF)約2mlとリグノフェノール誘導体約1mgを試験管に加え、タッチミキサーにて攪拌し、完全に溶解させた。その後、希薄なp-クレゾール・THF溶液を内部標準物質として一滴加え、再度タッチミキサーで攪拌し完全に均一化した。測定は、SHIMADZU LC10を用いて以下の条件で行った。

カラム: Shodex FK804, 803, 802, 801

溶媒: THF

流速: 1ml/分

圧力: 28~30kg/cm²

検出器: UV(280)

レンジ: 0.32

サンプル量: 150μl

検量線は基準物質としてポリスチレン390000、233000、100000、25000、9000、4000、2200、760、474、390、266、ビスフェノールA及びp-クレゾールを用い作成した。

【0042】(4) 結果

(4-1) 各種フェノール誘導体/95%リン酸を用いた処理後におけるリグノセルロース混合物の収率
フェノール誘導体の収着と95%リン酸処理後(相分離処理)におけるリグノセルロース混合物の収率を以下の表1に示す。

【0043】

【表1】

表1:

フェノール誘導体の種類	収率(最初の本粉に対する%)	
	ヒノキ	ブナ
p-クレゾール	98.4	77.4
2,6-キシレノール	98.9	81.1
2,4-キシレノール	92.5	80.2
2-メトキシフェノール	—	—
2,6-ジメトキシフェノール	97.8	80.9
カテコール	93.9	75.1
レゾルシノール	—	—
ホモカテコール	82.1	73.8
ピロガロール	85.2	56.2
フロログルシノール	98.9	104.4

【0044】(4-2) 各種フェノール誘導体/95%リン酸を用いた処理後における、アセトン可溶ジエチルエーテル不溶画分の収率

各種フェノール誘導体/95%リン酸を用いた処理後に

おける、アセトン可溶ジエチルエーテル不溶画分の収率を以下の表2及び表3に示す。

【0045】

【表2】

表 2 :

フェノール誘導体の種類	収率 (相分離処理した木粉に対する%)	
	ヒノキ	ブナ
p-クレゾール	11.6	21.1
2, 6-キシレノール	26.7	23.0
2, 4-キシレノール	16.0	19.3
2-メトキシフェノール	—	—
2, 6-ジメトキシフェノール	—	—
カテコール	13.0	17.3
レゾルシノール	—	—
ホモカテコール	25.5	23.0
ピロガロール	8.2	3.8
フロログルシノール	8.1	23.1

【0046】

【表3】

表 3 :

フェノール誘導体の種類	収率 (クラークソンリグニンに対する%)	
	ヒノキ	ブナ
p-クレゾール	36.3	70.9
2, 6-キシレノール	86.8	79.5
2, 4-キシレノール	48.6	66.0
2-メトキシフェノール	—	—
2, 6-ジメトキシフェノール	—	—
カテコール	40.1	55.4
レゾルシノール	—	—
ホモカテコール	68.8	72.3
ピロガロール	15.6	9.1
フロログルシノール	26.3	102.8

【0047】(4-3) 各種フェノール誘導体/95%リン酸を用いた処理後における、アセトン可溶ジエチルエーテル不溶画分の特徴

各種フェノール誘導体/95%リン酸を用いた処理後における、アセトン可溶ジエチルエーテル不溶画分の平均

分子量を以下の表4に示す。分子量の算出に用いたGPCの測定結果を図1(ヒノキ)及び図2(ブナ)に示す。

【0048】

【表4】

表 4 :

フェノール誘導体の種類	平均分子量 [Mw (Mw/Mn)]	
	ヒノキ	ブナ
p-クレゾール	9983(2.7)	4704(2.0)
2, 6-キシレノール	15133(2.4)	5418(1.9)
2, 4-キシレノール	20418(4.0)	10898(3.0)
2-メトキシフェノール	—	—
2, 6-ジメトキシフェノール	—	—
カテコール	4782(1.6)	3888(1.4)
レゾルシノール	—	—
ホモカテコール	5500(1.7)	4306(1.5)
ピロガロール	4234(1.4)	3357(1.3)
フロログルシノール	7785(1.9)	7979(2.3)

【0049】(4-4) アセチル処理後におけるアセトン可溶ジエチルエーテル不溶画分の収率

アセチル処理後におけるアセトン可溶ジエチルエーテル

不溶画分の収率を以下の表5に示す。

【0050】

【表5】

表5:

フェノール誘導体の種類	収率 (アセトン可溶ジエチルエーテル 不溶画分に対する%)	
	ヒノキ	ブナ
p-クレゾール	—	—
2, 6-キシレノール	120.0	114.0
2, 4-キシレノール	122.1	111.5
2-メトキシフェノール	—	—
2, 6-ジメトキシフェノール	—	—
カテコール	135.4	128.4
レゾルシノール	—	—
ホモカテコール	132.5	129.0
ピロガロール	140.2	143.0
フロログルシノール	127.4	124.3

【0051】(4-5)熱機械分析(TMA)の結果
各種フェノール誘導体/95%リン酸処理リグノセルロース、アセトン可溶ジエチルエーテル不溶画分、及びアセチル化後のアセトン可溶ジエチルエーテル不溶画分のTMA曲線の測定結果を図3～図5に示す。フェノール誘導体の収着と95%リン酸処理後(相分離処理)におけるリグノセルロース混合物のTMAパターンでは、150～200℃の温度領域に相転移点が認められた。これらの相転移点は、相分離処理試料から抽出したリグノフェノール画分の相転移点と一致しており、リグノフェノール誘導体に変換体総体(フェノール誘導体とリン酸で処理したリグノセルロース混合物)の可塑性に重要な寄与をもたらしていることが示される。

【0052】実施例2:リグノセルロース系組成物から成る成形体の調製と評価

(1)リン酸系相分離処理 (Phosphoric acid treatment)

脱脂試料1gにリグニンC₉単位当たり3mol倍量の各種フェノール誘導体(p-クレゾール、グアイアコール、カテコール、又はフロログルシノール)のアセトン溶液を加え、浸漬後、攪拌下にてアセトンを完全留去し、均一収着試料を調製した。収着試料に95%リン酸10mlを加え、50℃で1時間激しく攪拌した後、混合物を大過剰の水に投入、不溶解区分を遠心分離(8800 r.p.m., 8分, 5℃)にて回収、脱酸し、凍結乾燥し、リグノセルロース系複合試料を得た。

<成形条件>

試料	圧力 (kgf)	速度 (℃/分)	温度 (最初-最後)(℃)	ホールディング 時間(分)
オリジナル	50	1.5	70~180	0
アセテート	50	1.5	70~130, 150	0
ヒドロキシ メチル化	50	1.5	70~180	20

【0057】(5)各種試験(Test)

吸水試験(Water adsorption)

各種リグノセルロース系複合成型体をステンレス製ネットに置き、成型体の底面から3cmの深さまで水を張った容器に沈めた。成型体が浮上する場合には、成型体の上面から1～2mm上にステンレス製ネットを設置し、それ以

【0053】(2)アセチル化処理 (Acetylation)

リグノセルロース系複合試料7gをピリジン70mlに分散後、無水酢酸70mlを加え、攪拌下96時間反応させた。反応後、混合物を5℃の冷水3Lに滴下、不溶解区分を遠心分離(8800 r.p.m., 8分, 5℃)にて回収、5℃の冷水にて洗浄後、凍結乾燥した。

【0054】(3)メチロール化処理 (Hydroxymethylation)

リグノセルロース系複合試料7gに0.5NのNaOH140mlを加え、約30分間攪拌、分散後、1L容三ツ口フラスコに移し、攪拌しながら5倍に希釈した。環流管を取付け、窒素雰囲気下、37%ホルムアルデヒド溶液(リグノフェノール芳香核の80mol/C₉倍)を加え、湯浴中にて60℃で3時間反応させた。反応後、混合物を1NのHClにてpH2に酸性化、生じた沈殿を遠心分離(8800 r.p.m., 10分, 5℃)にて回収、脱酸後、凍結乾燥した。得られたメチロール化体は-80℃にて保存した。

【0055】(4)成型法 (Molding)

リグノセルロース系複合試料(オリジナル)およびそのアセチル化体、メチロール化体500mgをそれぞれ成型器(10mm径)で予備成形後、SHIMADZU フローテスターCFT-500Dの加熱圧縮シリンダ(10mm径)に入れ、以下の成形条件にて成形した。

【0056】

【表6】

上の浮上を抑制した。室温にて60分間水に浸漬後、成型体を取り出し、ろ紙上で転がして表面の水分を手早く除去した。60℃にて3日間乾燥させた。その際、吸水前、吸水後、乾燥後の重量および寸法を測定し、以下の式(1)、(2)を用いて吸水率Aw%、体積膨張率Vol%を求めた。

$$【0058】Aw\%=(Wt'-Wt)/Wt \times 100 \quad (1)$$

$$Vol\%=(Vol'-Vol)/Vol \times 100 \quad (2)$$

Aw% : 吸水率 (% to sample weight)

Wt : 試料重量 (g)

Wt' : 吸水試験後の試料重量 (g)

Vol% : 体積膨張率 (% to sample volume)

Vol : 試料体積 (cm³)

Vol' : 吸水試験後(下記表のウェットの欄)または再乾燥後(下記表のドライの欄)の試料体積 (cm³)

【0059】硬さ試験 (Brinell Hardness)

SHIMADZU AG-1 10kNにてJIS2117に準じて行った。各種

リグノセルロース系複合成型体の上面中央部に直径10mmの硬球を0.5mm/分の速度で圧入し、硬球が1/πmm=0.32mmの深さまで陥入するのに必要な荷重P(N)を測定し、以下の式(3)を用いて硬さH_B(MPa)を測定した。

$$H_B=P/10 \quad (3)$$

H_B : ブリネル硬さ (MPa)

P : 荷重 (N)

【0060】(6) 結果
結果を以下の表に示す。

【0061】

【表7】

	密度 (g/cm ³)	吸水率 (%)	体積膨張率 (%)		硬さ (Brinell hardness) (MPa)
			ウェット	ドライ	
ポリサッカロイド-リグノ-					
p-クレゾール(オリジナル)	1.01	7.9	-	-	-
p-クレゾール(アセテート)	0.99	1.8	0.6	-0.7	31.9
<70~130℃>					
p-クレゾール(アセテート)	1.21	0.8	0.6	-0.7	-
<70~150℃>					
p-クレゾール	0.71	17.3	13.1	-1.8	18.2
(ヒドロキシメチル化)					
グアイアコール	0.76	71.9	23.4	-0.5	-
(ヒドロキシメチル化)					
カテコール	0.67	93.9	15.7	2.2	-
(ヒドロキシメチル化)					
フロログリシノール	0.60	120.1	18.9	3.7	-
(ヒドロキシメチル化)					
MDF	0.57	-	-	-	-
ヒノキ	0.47	81.6	9.4	-2.3	木口面 12.5 板目面 8.9 根目面 6.9

【0062】

【発明の効果】本発明によれば、森林資源のリグノセルロース複合体構造の構成成分であるリグニンとセルロースの両方を繰返し有効利用できる新規な組成物を提供

することができ、森林資源を有効に利用することが可能になる。また、本発明によれば、上記組成物から、リグニン成分をリグノフェノール誘導体として回収することができ、森林資源のリグニン成分を有効に利用すること

ができる。

【図面の簡単な説明】

【図1】図1は、分子量の算出に用いたGPCの測定結果（ヒノキ）を示す。図1において、（1）はリグノ-2, 6-キシレノール、（2）はリグノ-2, 4-キシレノール、（3）はリグノ-カテコール、（4）はリグノ-ホモカテコール、（5）はリグノ-ピロガロール及び（6）はリグノ-フロログルシノールを示す。

【図2】図2は、分子量の算出に用いたGPCの測定結果（ブナ）を示す。図1において、（1）はリグノ-2, 6-キシレノール、（2）はリグノ-2, 4-キシレノール、（3）はリグノ-カテコール、（4）はリグノ-ホモカテコール、（5）はリグノ-ピロガロール及び（6）はリグノ-フロログルシノールを示す。

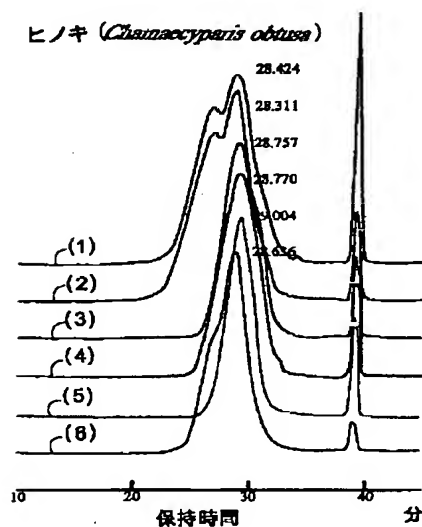
【図3】図3は、各種フェノール誘導体/95%リン酸処理リグノセルロースのTMA曲線の測定結果を示す。図3において、（1）はリグノ-2, 6-キシレノール、（2）はリグノ-2, 4-キシレノール、（3）は

リグノ-カテコール、（4）はリグノ-ホモカテコール、（5）はリグノ-ピロガロール及び（6）はリグノ-フロログルシノールを示す。

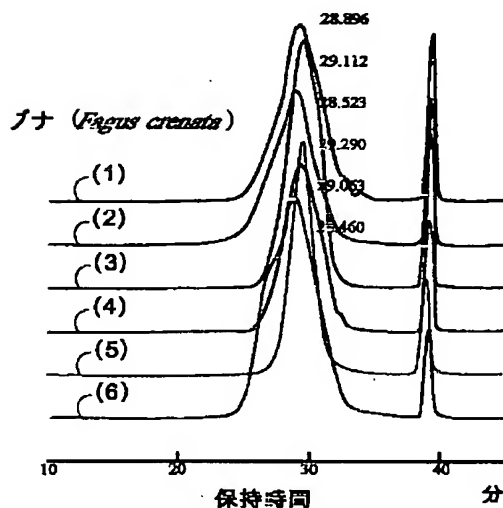
【図4】図4は、アセトン可溶ジエチルエーテル不溶画分のTMA曲線の測定結果を示す。図4において、（1）はリグノ-2, 6-キシレノール、（2）はリグノ-2, 4-キシレノール、（3）はリグノ-カテコール、（4）はリグノ-ホモカテコール、（5）はリグノ-ピロガロール及び（6）はリグノ-フロログルシノールを示す。

【図5】図5は、アセチル化後のアセトン可溶ジエチルエーテル不溶画分のTMA曲線の測定結果を示す。図5において、（1）はリグノ-2, 6-キシレノール、（2）はリグノ-2, 4-キシレノール、（3）はリグノ-カテコール、（4）はリグノ-ホモカテコール、（5）はリグノ-ピロガロール及び（6）はリグノ-フロログルシノールを示す。

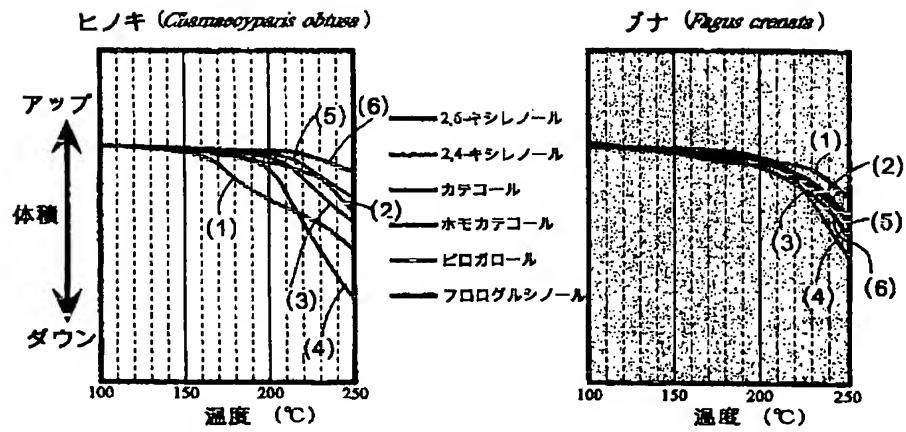
【図1】



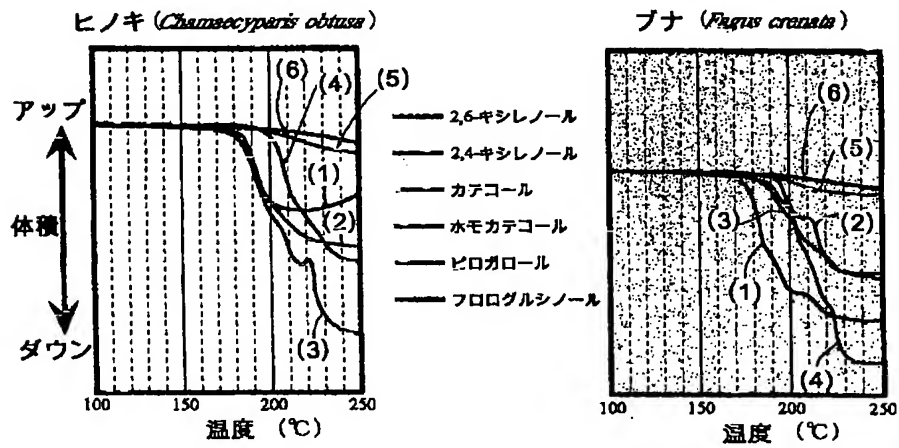
【図2】



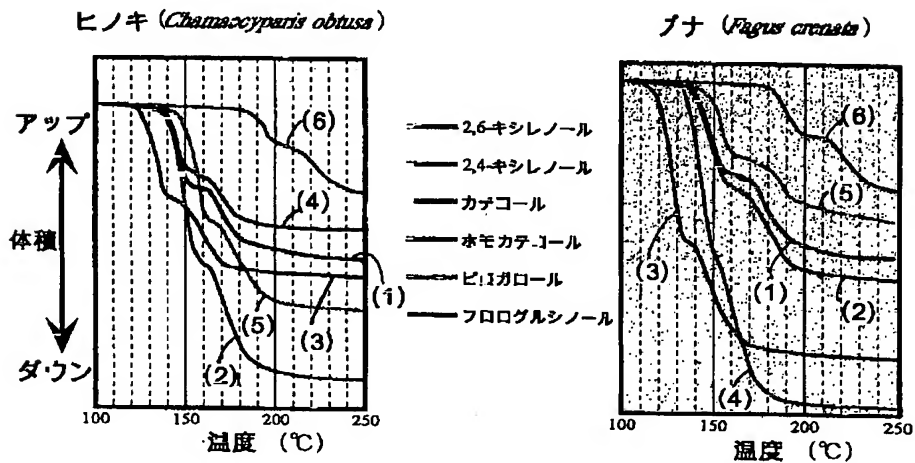
【図3】



【図4】

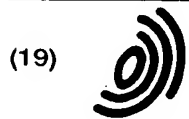


【図5】



フロントページの続き

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(54) NOVEL LIGNIN DERIVATIVE, MOLDINGS PRODUCED BY USING THE DERIVATIVE, AND PROCESS FOR THE PREPARATION THEREOF

(57) A process for the preparation of a novel lignin derivative, characterized by subjecting a lignophenol derivative having diphenylpropane units prepared by bonding the carbon atom of a phenol derivative ortho to the phenolic hydroxyl group to the benzylic carbon atoms of the phenylpropane basic units of lignin to treatment with an alkali capable of dissociating the above

hydroxyl group to thereby bond the oxygen atom of the hydroxyl group to the β -position carbon atom, thus forming an arylcoumaran derivative having arylcoumaran units constituted of the aromatic nuclei of lignin and coumaran skeletons bonded thereto.

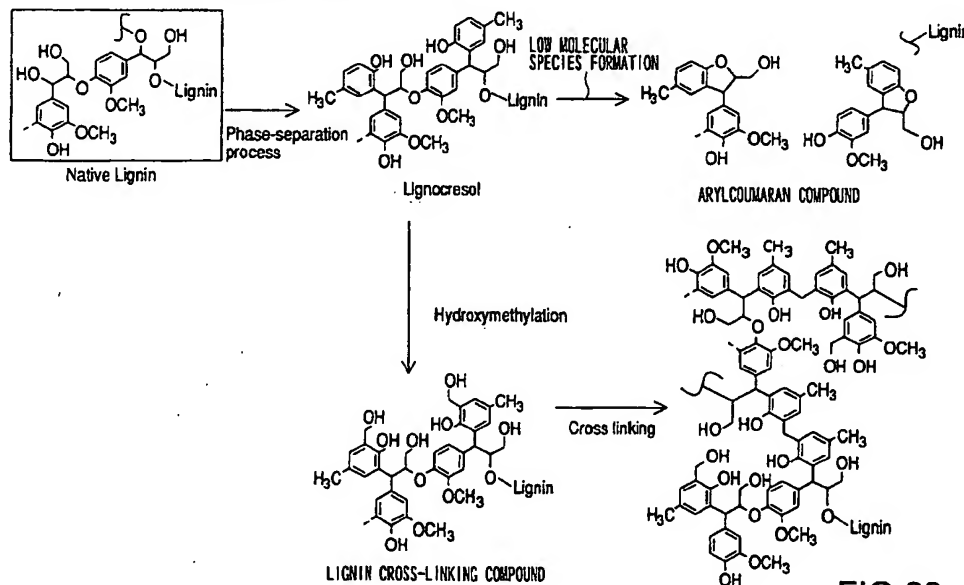


FIG.23

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Description

TECHNICAL FIELD

5 [0001] The present invention relates to a technical field of utilizing lignophenol derivatives obtained by phenol-derivatizing lignin, which are one component of timber. More particularly, the present invention relates to the technical field in which molded products are produced using novel materials obtained by further secondarily treating lignophenol derivatives with these materials and molding materials are recovered from the molded product for reuse.

10 BACKGROUND OF THE INVENTION

[0002] Recently, there has been increased an interest in forest resources that can be continuously used as industrial raw materials, instead of fossil resources, such as petroleum, coal and the like, which have been predicted to be depleted. Such a forest resource, i.e., a lignocellulose resource, is composed of hydrophilic carbohydrates, such as cellulose, hemicellulose and the like, and a hydrophobic lignin (polyphenol), which form the interpenetrating network (IPN) structure and an complicated complex in the cell wall. The lignocellulose resource imparts useful properties to various materials, because of the structure of the complex.

[0003] Two methods are known for utilizing the known lignocellulose resource, i.e. timber. One is a direct utilization of the lignocellulose material by cutting or machining the lignocellulose resource, i.e., the complex itself, and processing it into construction materials or furniture building materials having a predetermined shape, or processing the lignocellulose resource into chips or fibers for manufacturing molded products. The other is an indirect utilization of the lignocellulose material by extracting only cellulose, a component of the complex, and making a pulp of the product.

[0004] In view of the expected depletion of fossil resources in the future, the reuse of lignocellulose resources is important in the both utilization forms.

25 [0005] However, in the current situation, if a construction material is prepared according to the direct utilization method, it will have a predetermined shape and be comparatively large; therefore, treatments such as grinding and finely-dividing are usually necessary to reuse the construction material. In addition, thermosetting resins used in molded products are difficult to separate from wood chips and fibers. Therefore, in the direct utilization form, after the first use, a portion of the lignocellulose resource is discarded, in many cases without reuse.

30 [0006] Moreover, in the indirect utilization form, only cellulose is recovered and utilized to make a fiber or sheet.

[0007] Similarly, in the direct utilization form, the entire lignocellulose resource, i.e., cellulose and lignin, are not reused and, also in the indirect utilization form, lignin, which is one component of the lignocellulose resource, may be reused or not reused under in certain circumstances.

35 [0008] Lignin is an organic substance that exists in large amounts intermingled with cellulose. The present inventor considered the function of lignin as a complex constituting material and previously filed two applications that are directed to extraction of lignin from the lignocellulose resource in a functionalized form. The first application is Japanese Application No. 1-55686 (JP-A 2-233701) and the second application is Japanese Application No. 8-92695 (unpublished as of the filing date of this corresponding International application). The first application teaches methods of bonding a phenol derivative to the lignocellulose resource and, thereafter, contacting the lignocellulose resource with sulfuric acid, whereby lignin is separated from cellulose, because lignin has a bound phenol derivative. In addition, the second application teaches processes for manufacturing a novel cellulose-lignin molded product by using the hybrid lignin, which was provided in the first application, as a binder for a molded cellulose material.

DISCLOSURE OF THE INVENTION

45 [0009] Accordingly, an object of the present invention is to provide novel materials having improved functions that are formed by further secondarily-treating this hybrid lignin and to provide cellulose molded products utilizing these novel materials. In addition, another object is to provide methods for reusing the cellulose molded products by utilizing these novel materials.

50 [0010] In order to accomplish the aforementioned objects, the present inventor made the following inventions.

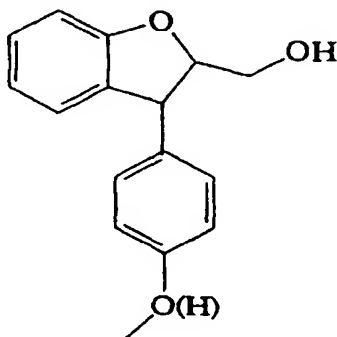
[0011] That is, a first invention is a novel process for producing a lignin derivative, which comprises using a lignophenol derivative containing a diphenylpropane unit formed by binding a carbon atom at an ortho-position relative to a phenolic hydroxyl group of a phenol derivative to a carbon atom at a benzyl-position of a phenylpropane fundamental unit of lignin, and binding an oxygen atom of the hydroxyl group to a β -positional carbon atom under alkali conditions, by which the hydroxyl group can dissociate, to obtain an arylcoumaran derivative containing an arylcoumaran unit in which a coumaran skeleton is bound to an aromatic ring of a phenylpropane unit of lignin. In this invention, the aforementioned phenol derivative is preferably p-cresol.

55 [0012] A second invention is a novel lignin derivative (hereinafter referred to as "an arylcoumaran derivative") rep-

resented by the following chemical formula and having an arylcoumaran unit in which a coumaran skeleton is bound to an aromatic ring of a lignin phenylpropane unit.

Chemical formula:

[0013]



[0014] A third invention is a process for producing a novel lignin derivative, which comprises heating a lignophenol derivative containing a diphenylpropane unit formed by binding an aromatic carbon atom of a phenol derivative to a carbon atom at a benzyl-position of a phenylpropane fundamental unit of lignin, with a cross-linking functional group forming compound under alkali conditions, by which the introduced phenolic hydroxyl group of a phenol derivative and/or a phenolic hydroxyl group originally existing in lignin can dissociate, to introduce a cross-linking functional group at an ortho-position and/or para-position of the phenolic hydroxyl group, thereby obtaining a lignin cross-linking derivative containing a diphenylpropane unit having a cross-linking functional group.

[0015] In this invention, preferably, the phenol derivative is p-cresol, the cross-linking functional group forming compound is formaldehyde and the cross-linking functional group is a hydroxymethyl group.

[0016] A fourth invention is a novel lignin derivative (hereinafter referred to as "a lignin cross-linking derivative") having a cross-linking functional group at an ortho-position and a para-position of a phenolic hydroxyl group of a lignophenol derivative containing a diphenylpropane unit formed by binding an aromatic carbon atom of a phenol derivative to a carbon atom at a benzyl-position of a phenylpropane fundamental unit of lignin. In this lignin derivative, a preferable cross-linking functional group is a hydroxymethyl group.

[0017] A fifth invention is molded products formed by molding fibrous, chip-like, or powdery substrate materials, characterized in that said molded products contain an arylcoumaran derivative.

[0018] This molded product has increased strength and water-resistance because of the connection of substrate molding materials using the arylcoumaran derivative. In addition, the arylcoumaran derivative can be easily extracted from a molded product using a solvent having affinity for the arylcoumaran derivative and can be separated from the molding material.

[0019] In this invention, the substrate molding material preferably is cellulose fiber, because cellulose fibers are readily available and are easily separated from the arylcoumaran derivative for reuse in a variety of ways.

[0020] A sixth invention is a molded product produced by molding fibrous, chip-like, or powdery substrate molding materials, characterized in that said molded product contains the aforementioned lignin cross-linking derivative.

[0021] This molded product has increased strength and water-resistance if molding substrate materials are bound by the lignin cross-linking derivative. Preferably, the lignin cross-linking derivatives are cross-linked, because cross-linking further increases strength and water-resistance.

[0022] A seventh invention is a method of treating a molded product, which comprises adding a solvent having affinity for this arylcoumaran derivative to a molded product containing the arylcoumaran derivative to recover the arylcoumaran derivative.

[0023] According to this invention, the arylcoumaran derivative is a binder material and can be reused and efficiently extracted and separated from a molded product. In addition, using this treatment, a molding substrate material can be reusable separated at the same time.

[0024] In this invention, the molding material preferably is cellulose fiber.

[0025] When the molding material is cellulose fiber, as a result of treatment with a solvent having affinity for a

lignophenol derivative, the cellulose fiber is also readily separated.

[0026] Timber, waste timber, end timber, herbaceous plants, agricultural waste and the like can be used as the lignocellulose material and thus, lignocellulose materials are efficiently used and reused.

[0027] Further, in this invention, the molding material preferably is cellulose fiber obtained by splitting a lignocellulose material.

[0028] When the molding material is a cellulose fiber obtained by splitting a lignocellulose material, a novel molded product is formed using a lignocellulose material. Moreover, cellulose fiber is readily available and is easily separated from a lignophenol derivative, which is utilized again in a variety of ways. In particular, when a lignophenol derivative is obtained from a lignocellulose material, both the cellulose component and the lignin component are efficiently used.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029]

FIG. 1 is the structural formula showing a phenylpropane unit of lignin.

FIG. 2 is a view showing a structure that may be derivatized at an α -position and a β -position of the phenylpropane unit of lignin.

FIGS. 3 (a) to 3 (d) are views illustrating examples in which a sub-unit is derivatized at an aromatic ring of the phenylpropane unit of lignin.

FIG. 4 is a view showing a first method for synthesizing a lignophenol derivative.

FIG. 5 is a view showing a second method for synthesizing a lignophenol derivative.

FIG. 6 is a view showing the reaction of lignin with a phenol derivative using concentrated sulfuric acid at an interface of a phenol derivative phase in a two phase phenol derivative/concentrated sulfuric acid solution.

FIG. 7 is a view showing a schematic in which a phenol derivative is selectively introduced at an α -position of a lignin sidechain.

FIG. 8 is a view showing a partial structure of lignin that has undergone structural conversion by introduction of a phenol derivative at an α -position of a lignin sidechain.

FIG. 9 (a) shows a UV spectrum of ground lignin and FIG. 9 (b) shows a UV spectrum of a lignophenol derivative.

FIG. 10 (a) shows a differential spectrum of ground lignin and FIG. 10 (b) shows a differential spectrum of a lignophenol derivative.

FIG. 11 (a) is an IR spectrum of ground lignin, FIG. 11 (b) is an IR spectrum of a lignin sulfate, and FIG. 11 (c) is an IR spectrum of a lignophenol derivative.

FIG. 12 (a) is an ^1H -NMR spectrum of an acetate compound of a lignophenol derivative and FIG. 12 (b) is an ^1H -NMR spectrum of an acetate compound of ground lignin.

FIG. 13 is a diagram showing the yields of lignophenol derivatives from lignocellulose materials of various origins.

FIG. 14 is a diagram showing elementary analysis results, an amount of introduced cresol, appearances, and a dissolving solvent for lignophenol derivatives obtained from lignocellulose materials of various origins.

FIG. 15 is a diagram showing the distribution of hydroxyl groups in lignophenol derivatives obtained from lignophenol materials of various origins.

FIG. 16 is a view showing a sub-unit of a lignophenol derivative that is used to synthesize an arylcoumaran derivative.

FIG. 17 is a view showing an arylcoumaran unit.

FIG. 18 is a view showing one example of an arylcoumaran unit obtained from a lignophenol derivative obtained by using p-cresol as a phenol derivative.

FIG. 19 is one example of a UV spectrum of an arylcoumaran derivative.

FIG. 20 is one example of an IR spectrum of an arylcoumaran derivative.

FIG. 21 is a view showing one example of a UV spectrum of a lignin cross-linking derivative.

FIG. 22 is a view showing one example of an IR spectrum of a lignin cross-linking derivative.

FIG. 23 is a view showing one example of a lignin structural conversion to a lignophenol derivative using p-cresol as a phenol derivative, an arylcoumaran derivative and a lignin cross-linking derivative.

FIG. 24 is a view showing principle aspects of a nucleus exchange method.

FIG. 25 is a view showing principle aspects of a periodate-oxidation treatment.

FIG. 26 is a view showing one example of the structural analysis in which a nucleus-exchange method and a periodate-oxidation method are applied to an arylcoumaran derivative.

FIG. 27 is a view showing steps for manufacturing a molded cellulose product using a secondary derivative.

FIG. 28 is a view showing steps for manufacturing a molded cellulose product using a secondary derivative.

FIG. 29 is a view showing transference of a secondary derivative upon removal by distillation of a solvent from a molded product, which solvent had solvated the secondary derivative.

FIG. 30 is a view showing steps for manufacturing a molded cellulose product using a secondary derivative.

FIG. 31 is a view showing steps for manufacturing a molded cellulose product using a secondary derivative.

FIG. 32 is a view showing steps for recovering a secondary derivative and a substrate constituting material from a molded product.

FIG. 33 is a view showing the steps of examples 1 to 3.

FIG. 34 is a diagram showing the properties of a lignophenol derivative and an arylcoumaran derivative, which is a derivative thereof.

FIG. 35 is a diagram showing the distribution of hydroxyl groups and the phenolic frequency for a lignophenol derivative and an arylcoumaran derivative, which is a derivative thereof.

FIG. 36 is a diagram showing the properties of a lignophenol derivative and a lignin cross-linking derivative, which is a derivative thereof.

FIG. 37 is a diagram showing the distribution of hydroxyl groups and the phenolic frequency for a lignophenol derivative and a lignin cross-linking derivative, which is a derivative thereof.

FIG. 38 is a view showing the state where a test piece is supported and a load is applied in a strength test.

FIG. 39 (a) is a graphical view showing Pmax; FIG. 39 (b) is a view showing MOE; FIG. 39 (c) is a view showing MOR.

FIG. 40 is a graphical view showing volumetric change rates of a molded cellulose product using a lignophenol derivative.

FIG. 41 is a graphical view showing volumetric change rates of a molded cellulose product using an arylcoumaran derivative.

FIG. 42 is a graphical view showing volumetric change rates of molded cellulose products using a lignophenol derivative, an arylcoumaran derivative and a lignin cross-linking derivative, respectively, by comparison.

FIG. 43 is a diagram showing a comparison of water-absorption and volumetric change rates for molded cellulose products using a lignophenol derivative, an arylcoumaran derivative and a lignin cross-linking derivative, respectively.

FIG. 44 is a diagram showing recovery rates of various derivatives from a molded product.

BEST MODES FOR CARRYING OUT THE INVENTION

[0030] Modes for carrying out the present invention will be explained in detail below.

[0031] In the present invention, an arylcoumaran polymer and a cross-linking lignin derivative are produced from a lignocellulose material containing lignin. The lignocellulose material containing lignin refers to the woody part of a plant. More particularly, various trees such as coniferous trees, broadleaf trees, and various herbaceous plants, such as rice, corn, beet and the like, can be used as a raw material for the lignocellulose material. In addition, although the lignocellulose material can be used in any form such as powder, chips or the like, a powder lignocellulose material has advantages for efficiently extracting the lignophenol derivative. Moreover, the lignocellulose material may be a waste timber or an end timber of a lignocellulose material, or a feed or an agricultural waste containing a lignocellulose material may be used.

[0032] In order to produce an arylcoumaran derivative or a lignin cross-linking derivative from the lignocellulose material, a phenol derivative must first be bound to the lignin of the lignocellulose material to produce a lignophenol derivative from the lignocellulose material, in which a phenol derivative is introduced exclusively at an α -position (benzyl-position) of a sidechain of a phenylpropane unit, which forms the lignin skeleton (this step is referred to as a first derivatization step).

[0033] In the present specification, the phenylpropane unit in lignin refers to a unit, of which the fundamental skeleton is a structure of the 9 carbons shown in the structural formula of FIG. 1. In this structure, the symbol -O(H) shown bound to an aromatic ring means that, in some cases, a hydrogen atom is bound to the oxygen atom of the aromatic ring, thereby forming a hydroxyl group and in some case, this oxygen atom together with another phenylpropane unit constitutes an ether linkage.

[0034] Within this phenylpropane unit is included an unit in which various structures shown in FIG. 2 are substituted at an α -position or a β -position of a sidechain of the fundamental unit of the aromatic ring. Also included is a unit in which an aromatic ring is bound to another substituent or another phenylpropane unit. Four examples are shown in FIGS. 3 (a) to (d) as examples of various aromatic rings having other substituents. The other aromatic rings include one or two methoxyl groups bound to an ortho-position relative to a phenolic or ethereal hydroxyl group, or one methoxyl group is bound to one or ortho-position and a carbon atom, which binds to the other fundamental unit that is bound to the other ortho-position.

[0035] Hereinafter, in the present specification and drawings, the aromatic rings derived from a phenylpropane unit of lignin, which are described in the specification and in the drawings, are intended to include all such variations.

[0036] In the present invention, a material having more functional features is formed by introducing the predeter-

mined phenol derivative at this α -position to decrease the structural irregularity of lignin and further secondarily-derivatized the resulting lignophenol derivative.

[0037] Currently, there are two methods for extracting lignin in a lignocellulose material as a lignophenol derivative. In this example, lignophenol derivative means a polymer containing a diphenylpropane unit in which a phenol derivative is introduced at an α -position of a sidechain of a phenylpropane unit of lignin via a C-C linkage. The amount and molecular weight of the introduced phenol derivative in this polymer varies depending upon the lignocellulose material used as a raw material and the reaction conditions.

[0038] The first method is a method described in the first application noted above (JP-A 2-233701).

[0039] In this method, for example, a lignocellulose material, such as wood powder or the like, is mixed with a liquid phenol derivative (such as cresol or the like) to dissolve the lignin in the phenol derivative. Then, concentrated sulfuric acid (for example, 72% sulfuric acid) is added to the lignocellulose material to mix and to dissolve the cellulose component. According to this method, the phenol derivative containing the dissolved lignin and the concentrated sulfuric acid containing the dissolved cellulose component form a two phase solution. Lignin dissolved in the phenol derivative only contacts the acid at an interface in which the phenol derivative phase contacts the concentrated acid phase. As a result, a cation at a sidechain α -position (benzyl-position), which is a highly reactive site of a lignin fundamental constituent unit and is produced by contact with the acid, binds to the phenol derivative. As a result, the phenol derivative is introduced at the α -position via a C-C linkage. In addition, a benzyl aryl ether linkage is made into low molecular species by cleavage. As a result, lignin is made into low molecular species and a lignophenol derivative, in which a phenol derivative is introduced at a benzyl-position of a fundamental constituent unit thereof, is produced in the phenol derivative phase (see FIG. 6). The lignophenol derivative is then extracted from this phenol derivative phase. The lignophenol derivative is obtained as a part of an aggregate of low molecular weight lignin that has been made into a low molecular species by cleavage of the benzyl aryl ether linkage in the lignin. Methods for introducing a phenol derivative at a benzyl-position via a phenolic hydroxyl group are known.

[0040] Extraction of the lignophenol derivative from the phenol derivative phase can be performed, for example, according to the following method. That is, the phenol derivative phase is added to a large excess of ethyl ether to obtain precipitates that are collected and dissolved in acetone. Acetone insoluble products are removed by centrifugation and the acetone-soluble products are concentrated. The acetone-soluble products are added dropwise to a large excess of ethyl ether and the precipitate fractions are collected. The solvent is distilled off from the precipitate fractions and the precipitate fractions are dried in a desiccator with phosphorus pentoxide to obtain a low-molecular weight crude lignophenol derivative containing the lignophenol derivative as a dried portion. In addition, the crude lignophenol derivative can be also obtained by removing the phenol derivative phase by simple distillation under reduced pressure. Moreover, the acetone-soluble products can be used as such as a lignophenol derivative solution in the secondarily-derivatized treatment.

[0041] In a second method, after a lignocellulose material is mixed with a solvent (for example, ethanol or acetone), which dissolves a solid or liquid phenol derivative, the solvent is distilled off as shown in FIG. 5 (phenol derivative sorbing step). Next, a concentrated acid is added to this lignocellulose material to dissolve the cellulose component. As a result, similar the first method, for lignin dissolved with the phenol derivative, a cation at a highly reactive site (sidechain α -position) of lignin that was produced by contact with the concentrated acid binds to the phenol derivative and the phenol derivative is introduced therein. In addition, lignin is made into low molecular weight species by cleavage of the benzyl aryl ether linkage. The properties of the resulting lignophenol derivative are not different from those obtained by the first method. Then, the lignophenol derivative is extracted by a liquid phenol derivative. Extraction of the lignophenol derivative from the liquid phenol derivative phase can be performed in the same manner as that of the first method. Alternatively, the whole reaction solution, after treatment with a concentrated acid, is placed into an excess of water and the insoluble fractions are collected, dialyzed and dried. Acetone or alcohol is added to this dried material and the lignophenol derivative is extracted. In addition, similar to the first method, this soluble fraction is added dropwise to an excess of ethyl ether or the like and the lignophenol derivative is obtained as an insoluble fraction.

[0042] Also in this method, similarly, an acetone-soluble product can be used as a lignophenol derivative solution for the secondarily-derivatizing treatment.

[0043] Of these two kinds of methods, the second method, which is a method for extracting and separating a lignophenol derivative with acetone or alcohol, is economical, because less phenol derivative is used. In addition, because this method can treat a large amount of lignocellulose material with a lessor amount of a phenol derivative, it is suitable for large scale synthesis of lignocellulose derivatives.

[0044] FIG. 7 shows a schematic in which a phenol derivative is selectively introduced at an α -position of the lignin sidechain by these methods. Introduction of the phenol derivative at a phenylpropane unit of lignin and the amount that is introduced can be confirmed by $^1\text{H-NMR}$. Selective introduction at an α -position of a sidechain of a phenylpropane unit also can be confirmed by $^1\text{H-NMR}$ and nucleus-exchange analysis.

[0045] Moreover, in FIG. 8, a step for converting natural lignin into a lignophenol derivative by these methods is represented by showing a change in a partial structure of the lignophenol derivative.

[0046] In addition, FIGS. 9 (a) and 9 (b) show a UV spectrum of a sample of milled wood lignin (hereinafter referred to as "ground lignin") obtained from defatted wood powder by a Bjorkman method and a lignophenol derivative (lignocresol) sample in the case in which cresol was introduced as the phenol derivative into the lignocellulose material. FIGS. 10 (a) and 10 (b) show an ionization differential spectrum (ΔE_i spectrum) of the respective samples of FIGS. 9 (a) and 9 (b). In FIGS. 9 (a) and (b) and FIGS. 10 (a) and (b), the lignophenol derivative shows a very sharp peak at 280 nm and 300 nm, respectively. Moreover, a shoulder peak that was observed at the longer wavelength side in the previous lignin samples was not seen at all in a lignocellulose derivative. This result shows that little complicated secondary structural change, such as generation of a conjugated system other than the selective phenolization at the sidechain α -position in the lignin phenylpropane unit, is produced in the first derivatized step and that, accordingly, the conjugated system disappears and the structural diversity is diminished. The lignocresol used was obtained by mixing 10 ml of p-cresol with 20 ml of 72% sulfuric acid per 1 g of wood powder and stirring at 25°C for 60 minutes according to the aforementioned first method. After measurement of the UV spectrum, the sample was dissolved in methyl cellulose. After measurement of the ΔE_i spectrum, measurements were performed using methyl cellulose and 1N sodium hydroxide solution.

[0047] FIGS. 11 (a) to 11 (c) show an IR spectrum (KBr method) of a ground lignin sample, a lignin sulfate sample (FIG. 11 (a)) prepared from defatted wood powder using a Tappi method, and the lignophenol derivative (lignocresol) (FIG. 11 (b)) used in FIGS. 9(b). IR spectrum of the lignophenol derivative has a very sharp absorption as compared with lignin sulfate prepared using only 72% sulfuric acid and it demonstrates that auto-condensation, which would make the molecule rigid, is not generated. In addition, little absorption is apparent near 1650 cm^{-1} , which would be attributable to a conjugated carbonyl group. Conversely, a strong absorption based on the adjacent 2H of a phenol ring is apparent near 800 cm^{-1} . This result is more consistent with that of the UV spectrum.

[0048] FIGS. 12 (a) and 12 (b) show an $^1\text{H-NMR}$ spectrum of the lignophenol derivative (lignocresol) used in FIGS. 9 (a) and 9 (b), the acetate thereof (FIG. 12 (a)), and the acetate of a ground lignin sample (FIG. 12 (b)). Although the acetoxy proton area (1.6-2.5ppm) overlaps with a methyl proton of the introduced cresol, it is clear that, from the signal pattern, the lignophenol derivative has many phenolic hydroxyl groups and still retains an aliphatic hydroxyl group. In addition, a methoxyl proton and an aliphatic sidechain proton (2.50-5.20 ppm) are clearly apparent and thus, it is believed that the irregularities of the natural lignin have been reduced. In addition, from the integrated values of the various peaks in these spectra, the amount of the aliphatic hydroxyl group and the aromatic hydroxyl group can be quantified and the amount of introduced phenol derivative (p-cresol in this spectrum) can be also quantified.

[0049] FIG. 13 shows the yields of lignophenol derivatives obtained by introducing p-cresol as a phenol derivative into lignocellulose materials (wood powder) of various origins (expressed as weight % relative to the lignin contained in wood powder and the yield includes introduced cresol). Little difference in the separating properties are observed among tree species for both coniferous trees and broadleaf trees. In addition, these lignophenol derivatives are obtained by using 10 ml of p-cresol and 20 ml of 72% sulfuric acid per 1 g of wood powder according to the aforementioned first method.

[0050] FIG. 14 shows the properties (elementary analysis results, the amount of introduced cresol, appearances and dissolving solvent) of various lignocresol samples produced by introducing cresol into lignocellulose materials (wood powder) of various origins (those obtained under the same conditions as those for the lignocellulose material of FIG. 10). As compared with the ground lignin sample, which is believed to have little structural change in the isolating step, the lignophenol derivative has 5% higher carbon content and 5% lower oxygen content based on cresol binding for both coniferous trees and broadleaf trees. Introduced cresol is about 25% (about 0.65 mol/C9) in coniferous trees and about 30% (about 0.9 mol/C9) in broadleaf trees and it has been proved that more than 90% of the binding positions are the sidechain α -position. In addition, the weight-average molecular weight is 3000-4000 in the lignophenol derivative derived from coniferous trees and is slightly lower in broadleaf trees. Further, the lignophenol derivative rapidly dissolves in various solvents, such as methanol, ethanol, acetone and the like.

[0051] In addition, the lignophenol derivative had a slightly pinkish-white appearance, even though it was treated with a concentrated acid and a large amount of cresol was introduced. This is greatly different from the lignin phenolized with a sulfuric acid or hydrochloric acid catalyst, which had a black color.

[0052] FIG. 15 shows the amount of hydroxyl group in lignophenol derivatives (lignocresol) obtained from various origins using the same conditions as those for the samples in FIGS. 10 (a) and 10 (b). The lignophenol derivative does not have a benzyl hydroxyl group at a sidechain α -position and on the other hand, the sidechain γ -positional hydroxyl group is retained in the same amount as that of a ground lignin. Phenolic hydroxyl groups are greatly increased as a result of cleavage of the benzyl aryl ether in lignin and introduction of cresol in the treating process.

(Lignophenol derivative as a starting material for synthesizing an arylcoumaran polymer)

[0053] A lignophenol derivative, which is used for synthesizing an arylcoumaran polymer of the present invention, requires that the carbon at an ortho-position relative to a phenolic hydroxyl group of introduced phenol derivative is

bound to a sidechain α - positional carbon of a phenylpropane unit of lignin. That is, the fundamental structure shown in FIG. 16 is required. In FIG. 16, the aromatic ring of the introduced phenol has no substituents other than hydrogen. However, in the present invention, the introduced phenol ring of the lignophenol derivative is not intended to be limited to such a structure and it may have other substituents. In the present specification, claims and drawings, the phenol derivative that is introduced into a phenylpropane unit is described and expressed in drawings is intended to include phenol derivatives having various substituents.

[0054] Because the phenolic hydroxyl group of such introduced phenols dissociates under alkali conditions and an arylcoumaran structure is formed by rearrangement with the adjacent groups, the phenol derivative for synthesizing a lignophenol derivative, which is then used to synthesize an arylcoumaran polymer of the present invention, simply requires that at least one ortho-position relative to one phenolic hydroxyl group is free, that is, there is no substituent at that position, because this ortho-position will become a site for binding to the main lignin structure. More particularly, monovalent phenol derivatives, such as phenol, alkylphenols, such as cresol and the like, methoxyphenol, naphthol and the like, divalent phenol derivatives, such as catechol, resorcinol and the like, and trivalent phenol derivatives, such as pyrogallol and the like, are appropriate, because these derivatives do not have any substituents at an ortho-position relative to a phenolic hydroxyl group.

[0055] Confirmation of the formation of such lignophenol derivatives can be confirmed by $^1\text{H-NMR}$ and nucleus exchange analysis.

(Lignophenol derivative as a starting material for synthesizing a cross-linking lignin derivative)

[0056] The lignophenol derivatives, which can be used to synthesize a cross-linking lignin derivative of the present invention, are not particularly limited. In the present invention, a cross-linking functional group is introduced into a site that is an ortho-position or para-position relative to the phenolic hydroxyl group, which introduction site inherently exists in the phenylpropane unit of lignin, because when the cross-linking functional group is introduced into any site of a diphenylpropane unit of a lignophenol derivative, a cross-linking lignin derivative is formed.

[0057] Increase in an introduced amount and adjustment of an introduced amount by introducing a cross-linking functional group also on the introduced phenol derivative side can be accomplished by selecting the phenol derivative to be introduced.

[0058] That is, because the cross-linking functional group is introduced at the ortho-position or para position relative to the phenolic hydroxyl group under alkaline conditions by which a phenolic hydroxyl group dissociates, when at least one of the ortho-position or the para-position relative to the phenolic hydroxyl group of the introduced phenol is free in a lignophenol derivative, the cross-linking functional group also will be introduced at the introduced phenol derivative side.

[0059] In order to produce the lignophenol derivative of the present invention, because the sidechain α -positional carbon of the lignin phenylpropane unit and the carbon that is ortho-position or para-position relative to phenol derivative phenolic hydroxyl group are bound together, in order to obtain a cross-linking lignin derivative when at least two sites of two positions and one para-position relative to one phenolic hydroxyl group are free, one site becomes a site for binding to the phenylpropane unit and thereafter, another cross-linking functional group introducing site can remain.

[0060] Conversely, if a lignophenol derivative in which a phenol derivative having substituents at two or more sites among an ortho-position and a para-position relative to the phenolic hydroxyl group is used, such as 2,4-xylenol, 2,6-xylenol and the like, because a cross-linking functional group introducing site is no longer present in the introduced phenyl derivative, only the cross-linking functional group will be introduced into the main lignin structure.

[0061] Therefore, by combining a phenol derivative having a cross-linking functional group introducing site and a different reactivity with a phenol derivative having no or a different introducing site number, or combining two or more of them, the number of sites for introducing a cross-linking functional group in a lignophenol derivative can be controlled and as a result, the cross-linking degree of the cross-linking lignin derivative can be controlled.

[0062] Preferred phenol derivatives, which can also introduce a cross-linking functional group at an introduced phenol derivative side, are phenol and cresol (particularly, m-cresol). In addition, preferred phenol derivatives, which do not introduce a cross-linking functional group into the introduced phenol derivative, are 2,4-xylenol and 2,6-xylenol.

(Preparation of an arylcoumaran derivative)

[0063] In order to obtain an arylcoumaran derivative from a lignophenol derivative, a lignophenol derivative having a carbon in an ortho position relative to the phenolic hydroxyl group of the aforementioned predetermined lignophenol derivative, i.e. a phenol derivative is bound to the carbon at a sidechain α -position of the main lignin structure, is treated under alkali conditions.

[0064] This alkali treatment step dissociates a phenolic hydroxyl group of the phenol derivative that was introduced at the sidechain α -position, forming a bond with the sidechain β -positional carbon and at the same time, cleaves the

β -aryl ether linkage. By this treatment, a coumaran structure represented by the structural formula below can be formed at the sidechain α -position. This treatment leads to etherification of the phenolic hydroxyl group of the introduced phenol derivative by formation of a bond between the phenolic hydroxyl group and the carbon of the introduced phenol derivative, and the appearance of a new phenolic hydroxyl group at a benzene ring of a main lignin structure. As a result, this alkali treatment also transfers a phenolic hydroxyl group (phenol activity) from an α -position-introduced phenol derivative to the main lignin structure.

[0065] More particularly, this alkali treatment is performed by dissolving a lignophenol derivative in an alkali solution, permitting the reaction to proceed for a period of time and, if needed, heating.

[0066] Alkali solutions used in this treatment may be any alkali solution as long as it can dissociate the phenolic hydroxyl group of the introduced phenol derivative in the lignophenol derivative, and the type and concentration of alkali conditions or the type of solvents and the like are not limited, because when the aforementioned dissociation of the phenolic hydroxyl group occurs under alkali conditions, a coumaran structure is formed by the adjacent groups.

[0067] For example, in the case of a lignophenol derivative in which p-cresol is introduced, an aqueous NaOH solution can be used. If treatment is performed at an alkali concentration of 0.5 to 2N for 2 hours, it has been confirmed that the degree of low-molecular species and the formation of arylcoumaran derivatives from the lignophenol derivative are slightly different depending upon the concentration of the alkali solution.

[0068] In addition, the lignophenol derivative will readily rearrange under alkali conditions and heating to form a coumaran structure. Conditions such as a temperature, pressure and the like when the heating is started can be set without particular limitation in a range for which the formation of an arylcoumaran derivative is not promoted. For example, an arylcoumaran derivative can be efficiently obtained by heating an alkali solution to a temperature of not lower than 100°C. In addition, an arylcoumaran derivative may be obtained more efficiently by heating an alkali solution to a temperature not lower than the boiling point thereof under pressure.

[0069] It has been proved that, if the heating temperature is increased, the production of low-molecular species by cleavage of the β -aryl ether linkage is promoted in the heating temperature range of 120°C to 140°C for identical alkali solutions and concentrations. In addition, it has been also proved that, as the heating temperature is increased, phenolic hydroxyl groups derived from an aromatic ring derived from the main lignin structure are increased and phenolic hydroxyl groups derived from an introduced phenol derivative are decreased, in the aforementioned temperature range. Therefore, the degree of low molecular species formation and the degree of transference of a phenolic hydroxyl group site from an α -position-introduced phenol derivative side to a phenol ring of the main lignin structure can be adjusted by the reaction temperature. That is, in order to promote low molecular species formation and obtain an arylcoumaran derivative in which more phenolic hydroxyl group sites are transferred from an α -position-introduced phenol derivative side to the main lignin structure, a higher reaction temperature is preferable. The heating temperature is preferably not lower than 80°C and not higher than 160°C. When the temperature is much lower than 80°C, the reaction does not proceed sufficiently and, when the temperature significantly exceeds 160°C, non-preferable reactions result. More preferably, the temperature is not lower than 100°C and not higher than 140°C. In addition, heating is preferably performed under pressure.

[0070] One example of such a treatment utilizes conditions under which an aqueous 0.5N NaOH solution is used as the alkali solution and the treatment is performed at 140°C for 60 minutes in an autoclave. In particular, these treatment conditions are preferably used for lignophenol derivatives that are derivatized with p-cresol.

[0071] In low molecular species formation treatment of a ligno-hybrid derivative in the alkali solution, for example, the reaction is stopped by cooling or the like, the pH is lowered to around 2 using a suitable acid, such as 1N hydrochloric acid or the like, to regenerate the phenolic hydroxyl group (as an OH group), and the resulting precipitates are centrifuged, washed under neutral conditions and after lyophilization, further dried over phosphorus pentoxide. As a result, an arylcoumaran derivative, i.e., a lignin-derived derivative having a coumaran skeleton, can be obtained.

[0072] An arylcoumaran derivative is a lignin derivative containing a structure (an arylcoumaran unit) in which a phenol ring is introduced at a sidechain α -positional carbon atom of an aromatic ring of a phenylpropane unit of lignin together with the phenylpropane unit and forms a coumaran skeleton as shown in FIG. 17. The weight-average molecular weight is preferably 500 to 2000. In addition, an arylcoumaran derivative having an arylcoumaran unit of 0.3 to 0.5 mol/C9 (fundamental unit) is preferable. An arylcoumaran derivative means both a monomer consisting of such an arylcoumaran unit and a polymer partially having a fundamental unit having an arylcoumaran unit (at least at an end part), including an arylcoumaran derivative that is a mixture of the monomer and the polymer. An arylcoumaran derivative may contain simple low-molecular species compounds derived via the cleavages of the benzyl aryl ether bond and β -aryl ether bond of lignophenols in the step for preparing this arylcoumaran derivative. Usually, the arylcoumaran derivative is obtained in a mixed state in which the mixture contains such low-molecularized compounds in addition to a monomer and a polymer in the alkali solution.

[0073] FIG. 18 shows one example of an arylcoumaran unit obtained from a lignophenol derivative using p-cresol as a phenol derivative.

(Structure of an arylcoumaran derivative)

[0074] The percentage of the coumaran skeleton and the phenolic aromatic ring in the thus obtained arylcoumaran derivative, the amount of introduced cresol, the amount of a hydroxyl group and the entire structure can be confirmed by a nucleus exchange method, $^1\text{H-NMR}$ or the like.

[0075] A UV spectrum (solvent: tetrahydrofuran) and an IR spectrum (KBr method) of an arylcoumaran derivative are shown in FIGS. 19 and 20.

(Preparation of a lignin cross-linking derivative)

[0076] A lignin cross-linking derivative refers to a derivative in which a cross-linking functional group is introduced at an ortho- and/or para-position relative to a phenolic hydroxyl group of a lignophenol derivative. The weight-average molecular weight is preferably 2000 to 10000 and the amount of introduced cross-linking functional group is preferably 0.3 to 1.5 mol/C9 unit. A hydroxymethyl group is preferable as the cross-linking functional group.

[0077] A lignin cross-linking derivative can be obtained by mixing a lignophenol derivative with a compound that can form a cross-linking functional group on the lignophenol derivative to react under conditions by which the phenolic hydroxyl group of the lignophenol derivative will dissociate.

[0078] The conditions under which the phenolic hydroxyl group of the lignophenol derivative will dissociate are usually formed in a suitable alkali solution. The type and concentration of the alkali conditions and the solvent can be used without limitation so long as the phenolic hydroxyl group of the hybrid compound dissociates. For example, a 0.1N aqueous sodium hydroxide solution can be used.

[0079] The cross-linking functional group that is introduced into the lignophenol derivative is not particularly limited. Any cross-linking functional group may be used so long as it can be introduced at an aromatic ring of the main lignin structure or at an aromatic ring of the introduced phenol derivative. More particularly, the cross-linking reactive group can be introduced into the aforementioned aromatic compound by mixing a polymerizable compound, such as formaldehyde, glutaraldehyde, diisocyanate and the like, with these compounds under conditions in which the phenolic hydroxyl group in a lignophenol derivative can dissociate. Because the β -aryl ether linkage also dissociates under such conditions, the lignophenol derivative is low-molecular species.

[0080] Upon mixing of the lignophenol derivative with the cross-linking functional group forming compound, in order to efficiently introduce the cross-linking functional group, a cross-linking functional group forming compound is preferably added at 1 or more mole-amount with respect to the aromatic ring of the lignin phenylpropane unit in the lignophenol derivative and/or the introduced phenol ring. More preferably, it is added at 10 or more mole-amount and, further preferably, 20 or more mole-amount.

[0081] Then, the cross-linking functional group is introduced into the introduced phenol ring under conditions in which the phenol derivative and the cross-linking functional group forming compound are present in alkali solution, or by heating if necessary. While the heating conditions are not particularly limited so long as a cross-linking functional group is introduced, the range of 40°C to 100°C is preferable. When the temperature is lower than 40°C, the cross-linking functional group forming compound reaction rate is very low and, when the temperature is higher than 100°C, side reactions result in addition to the introduction of the cross-linking functional group into the lignin, such as the cross-linking functional group forming compound reacting with itself. The range of 50°C to 80°C is more preferable and about 60°C is further preferable.

[0082] The reaction is stopped by cooling the reaction solution and acidifying with hydrochloric acid having a suitable concentration (for example, around pH 2); the reaction mixture is washed and dialyzed to remove the acid and unreacted cross-linking functional group forming compound. After dialysis, the sample is recovered by lyophilization or the like. If needed, the sample is dried over phosphorus pentoxide under reduced pressure.

(Structure of a lignin cross-linking derivative)

[0083] Whether the desired functional group has been introduced at the o-position or p-position relative to the phenolic hydroxyl group in the thus obtained lignin cross-linking derivative or not, and the entire structure can be confirmed by a nucleus exchange method, $^1\text{H-NMR}$ or the like.

[0084] A UV spectrum (solvent: tetrahydrofuran) and an IR spectrum (KBr method) of an arylcoumaran derivative are shown in FIGS. 21 and 22.

[0085] In addition, in one example of structural conversion of lignin, a lignophenol derivative, an arylcoumaran derivative and a lignin cross-linking derivative are shown in FIG. 23. In this example, p-cresol is used as a phenol derivative and a hydroxymethyl group is introduced as the cross-linking functional group.

(A method for confirming the properties of the lignophenol derivative, the arylcoumaran derivative and the cross-linking lignin derivative)

1. Confirmation of production of a coumaran unit and quantification of the distribution of the phenolic aromatic ring

[0086] The structure of an arylcoumaran derivative, or more particularly, the structure of an arylcoumaran fundamental unit, can be confirmed by comparing, before and after the alkali treatment, the frequency of the phenolic properties of the cresol ring and the lignin aromatic ring (mainly guaiacyl ring) by a ring conversion method combined with a periodate oxidation treatment.

[0087] A nucleus exchange method is a procedure by which a phenol monomer is quantitatively obtained from a phenol polymer, such as lignin, in a medium in which boron trifluoride (BF₃) and a large excess of phenol are present. The reaction of lignin with phenol in this nucleus exchange method introduces medium phenol at a sidechain α -position of lignin side to form a diphenylmethane type structure between a lignin aromatic ring and to further liberate this lignin aromatic ring as guaiacol or the like and repeated DPM formation of the remaining introduced medium phenol and liberation of a phenol ring. By utilizing the quantitative properties of this reaction, the position at which the phenyl ring is bound to an aliphatic sidechain in a phenylpropane unit of lignin can be determined.

[0088] In addition, it is known that periodate treatment quantitatively destroys the phenolic aromatic ring as shown in FIG. 25. When combined with the nucleus exchange method utilizing this procedure, the distribution of hydroxyl groups in a lignin aromatic ring and an α -position introduced phenol ring can be analyzed.

[0089] A method for measuring the frequency of the phenolic properties of the cresol ring and the guaiacyl ring and confirming production of the coumaran unit by utilizing a nucleus exchange method is provided below.

[0090] The following explanation provides one example for analyzing the lignocresol exemplified in FIG. 23, which is one kind of a lignophenol derivative using p-cresol as a phenol derivative, and an arylcoumaran derivative shown in FIG. 26 that is obtained by using this lignophenol as a starting material is explained. By utilizing this analyzing example, the fundamental unit of other arylcoumaran derivatives can be similarly confirmed. The symbols shown in FIG. 26 represent the following structures:

Gp: Phenolic guaiacyl ring
 GE: Ether type guaiacyl ring
 CP: Phenolic cresol ring introduced at an α -position
 CE: Ether type cresol ring introduced at an α -position

[0091] As shown in FIG. 26, when this lignophenol is nucleus exchange-treated, because cresol has a cresol ring at an α -position at high frequency, a DPM type structure is formed between guaiacyl ring-cresol ring from initiation. Therefore, the lignophenol is rapidly nucleus exchanged and, regardless of the phenolic properties of the guaiacyl ring, the guaiacyl ring and the cresol ring are liberated as a monomer. That is, cresol liberation is of all CP origin and guaiacyl ring (guaiacol and catechol) liberation is of GP and GE origin.

[0092] However, when the periodate treatment is performed, because cresol (CP) is all phenolic, the cresol ring is destroyed and, at the same time, the phenolic guaiacyl ring is also destroyed. An ether type guaiacyl ring (GE) remains and liberation by a nucleus exchange method provides only the non-phenolic guaiacyl ring (GE).

[0093] On the other hand, when an arylcoumaran derivative is produced as a low-molecular species, this lignocresol is directly nucleus exchange-treated by the alkali treatment and the same number as that of the hybrid compound before the alkali treatment of a guaiacyl ring and a cresol ring are liberated. When this low-molecular species compound is nucleus exchange-treated after the periodate treatment, only an ethereal cresol ring (CE) forming an arylcoumaran structure is liberated.

[0094] Therefore, whether α -position-introduced cresol is bound to the β -carbon in the alkali treatment or not (whether a coumaran unit was formed or not) and whether the phenolic properties were newly manifested in the guaiacyl ring or not, i.e., whether a coumaran structure was produced or not, can be confirmed by the type of liberated phenols that are obtained by performing the 4 kinds of nucleus exchange treatments, either alone, and either before and after the alkali treatment, and the periodate oxidation decomposition and the treatment combined with nucleus exchange and by the difference in yields thereof.

[0095] More particular procedures are indicated below.

(Preparation of a lignophenol derivative sample and an arylcoumaran derivative sample)

[0096] Each sample used for the nucleus exchange treatment and the periodate treatment was prepared as follows:

[0097] The lignophenol derivative sample was prepared as follows: After p-cresol was adsorbed onto wood powder, 72% sulfuric acid was added to treat at room temperature for 60 minutes, all the reaction solution was placed into an

excess of water and the insoluble fractions were collected by centrifugation, dialyzed and dried. The dried material was extracted with acetone, the soluble fraction was added dropwise to an excess of ethyl ether, and the resulting insoluble fraction was dried on P_2O_5 .

[0098] An arylcoumaran derivative sample was prepared by treating the lignophenol derivative (lignocresol) obtained as described above in a 0.5N aqueous NaOH solution at 140°C for 60 minutes, acidifying to pH 2 with 1N hydrochloric acid, washing the precipitates under neutral conditions, lyophilizing and drying on P_2O_5 .

(Preparation of a nucleus exchange reagent)

[0099] The reagent used for the nucleus exchange treatment was a mixture of phenol (Nakalai Tesque, Inc., extra pure reagent), xylene (Nakalai Tesque, Inc., extra pure reagent) and boron trifluoride-phenol complex (contained at 25%, Nakalai Tesque, Inc., extra pure reagent) at a volume ratio of 19:10:3.

(Nucleus exchange treatment)

[0100] A suitable amount of a lignophenol derivative or an arylcoumaran derivative sample was placed into a 3 ml stainless steel microautoclave already containing two steel balls for stirring, and 2 ml of a nucleus exchange reagent was added thereto. The autoclave was sealed and stirred for 10 minutes or more to homogenize the contents. Thereafter, the autoclave was immersed into an oil bath at 110°C and heated for 4 hours. During heating, the contents in the autoclave were stirred every 30 minutes.

[0101] After completion of the reaction, the autoclave was taken out of the oil bath, placed into water, and the reaction was stopped by cooling. Silicone oil adhered to the autoclave was wiped completely clean, the autoclave was opened, and the contents were transferred into a 100 ml beaker by washing with a small amount of diethyl ether (Wako Pure Chemical Industries Co., Ltd., extra pure reagent). A solution of a known amount of an internal standard substance (dibenzyl (Tokyokasei Kogyo Co., Ltd. extra pure reagent)) in benzene (Wako Pure Chemical Industries Co., Ltd., extra pure reagent) (12 mg/ml) was added thereto, the ether-insoluble was filtered with a glass fiber filter (Whatman GF/A 4.5 cm) and washed a few times with diethyl ether. The filtered material was transferred to a 300 ml separating funnel and a saturated sodium chloride solution and sodium chloride (Nakalai Tesque, Inc., extra pure reagent) were added with vigorous shaking to inactivate the BF_3 . The ether layer was recovered and concentrated to about 10 ml relative to 1 ml of a reagent. The concentrated material was transferred into a 50 ml Teflon-liner screw vial, anhydrous sodium sulfate (Wako Pure Chemical Industries Co., Ltd., extra pure reagent) was added and dehydrated overnight at the cool place.

(Quantification of product)

[0102] 50 μ l of the dehydrated ether solution was placed into a 1 ml Teflon-liner screw vial, one droplet of pyridine (Wako Pure Chemical Industries Co., Ltd., extra pure reagent) and 100 μ l of Bis (trimethylsilyl) trifluoroacetamide, BSTFA (Aldrich, 99+%) were added thereto, and allowed to stand at room temperature for 1 hour to perform the TMS treatment. A TMS derivative of a liberated monomer was quantified by gas chromatography (GLC). The produced amount was calculated from a calibration curve for a monomer. The GLC conditions were as follows:

Apparatus: YANAGIMOTO G-3800

Column: Crosslinked methyl silicon capillary column (Quardrex s2006:0.25 mm I.D. 50m length 0.25 μ m Film thickness)

Sensitivity: 10⁻¹

Attenuator: 1/1

Column temp.: Initial temp.: 130°C, 6min.

: Rate: 3.0°C/min.

: Final temp.: 190°C

Injection temp.: 230°C

Carrier gas: Helium

Detector: FID

(Preparation of a periodate oxidizing reagent)

[0103] 500 ml of a solution of glacial acetic acid (Wako Pure Chemical Industries Co., Ltd., extra pure reagent): water (3:2 (v/v)) was added to 15 g of sodium methaperiodate (Nakalai Tesque Inc, extra pure reagent). The periodate oxidizing reagent was placed in a brown reagent bottle and stored at 4°C.

(Periodate oxidation treatment)

[0104] 1 ml of glacial acid was added to 100 mg of a lignophenol derivative or an arylcoumaran derivative sample to dissolve the sample as soon as possible, and 15 ml of a periodate oxidizing reagent was added with stirring to perform the treatment at 4°C for 3 days. After treatment, the mixture was added dropwise into 200 ml of ice-cooled water under stirring, the resulting precipitates were centrifuged (5°C, 3500 rpm, 10 min.) to recover the precipitates, washed with cool water, and lyophilized to dry over P₂O₅ in order to obtain the periodate oxidation treatment sample. This sample was nucleus exchange-treated as described above, and subsequently the product was quantified according to the aforementioned product quantifying method.

2. Quantification of the amount of introduced cresol and hydroxyl group

[0105] Quantification of the amount of introduced cresol and hydroxyl group was analyzed by ¹H-NMR.

[0106] The hybrid compound and the arylcoumaran derivative were prepared as samples as is or as an acetylated material.

[0107] Each 20 mg of the sample and 3 mg of p-nitrobenzaldehyde (PNB) as an internal standard were weighed precisely into a 1 ml vial, which was completely dissolved in deuterated pyridine:deuterated chloroform (1:3) (an acetylation sample was dissolved only with deuterated chloroform) using an Eppendorf pipette to obtain a sample for measurement.

[0108] Measurement by ¹H-NMR was performed using an R-90H Fourier transformation type nuclear magnetic resonance apparatus manufactured by HITACHI. From the integrated curve of the resulting chart, the amount of introduced cresol was calculated according to the following calculating method.

(Analysis)

[0109] The following is an example of an analysis that can be applied to the lignocresol produced using cresol as a phenol derivative, an arylcoumaran derivative produced by further treating this lignocresol and a cross-linking lignin derivative.

(1) Quantification of the amount of introduced cresol

[0110] ¹H-NMR was performed using the HITACHI R-90H Fourier transformation type nuclear magnetic resonance apparatus. From the integrated curve for the resulting chart, the amount of introduced cresol was obtained according to the following calculating method.

$$I\text{ wt}\% = \{Pwt/Pm \times Pn/Pi \times Ci/Cn \times (Cm-1)\} / Lwt \times 100$$

$$I\text{ mol/C9} = \{Iwt\% / (Cm-1)\} / \{(100-Iwt\%) / Lm\}$$

[0111] Wherein:

Iwt%: Amount of introduced cresol (wt%)

Pwt: Weight of PNB (mg)

Pn: Number of aromatic ring Hs in PNB (4)

Pi: Integrated value of an area indicating an aromatic ring 4H signal in PNB (8.40-7.80 ppm)

Ci: Integrated value of an area indicating a methyl group 3H signal in introduced cresol (2.40-1.60 ppm)

Cn: Number of protons of a methyl group introduced cresol (3)

Cm: Molecular weight of introduced cresol (108)

Lwt: Weight of lignocresol (hybrid derivative) (mg)

I mol/C9: Amount of introduced cresol (mol/C9)

Lm: Molecular weight of 1 unit of lignin (200)

(2) Quantification of the amount of hydroxyl group

[0112] Measurement of ¹H-NMR was performed using the same apparatus as the aforementioned apparatus based on the same sample preparing method. From the integrated curve for the resulting chart, the amount of a phenolic hydroxyl group and that of an aliphatic hydroxyl group were calculated according to the following calculating method.

[0113] Because the ^1H -NMR spectrum for an acetylated sample has an area indicating a phenolic acetoxyl proton signal (2.40-2.03 ppm) and an area indicating an aliphatic acetoxyl proton signal (2.03-1.60 ppm) that overlap with an area indicating a methyl proton signal of that introduced cresol (2.40-1.60 ppm), each integrated value was corrected according to the following equations:

$$\text{Aph} = \text{Aph}' - \text{Oph} \times \text{Aar} / \text{Oar}$$

$$\text{Aali} = \text{Aali}' - \text{Oali} \times \text{Aar} / \text{Oar}$$

Aph: An integrated value for an area indicating a phenolic acetoxyl proton signal (corrected value)

Aph': An integrated value for an area indicating a phenolic acetoxyl proton signal in an acetylated sample (corrected value)

Oph: An integrated value for an area (2.40-2.03 ppm) that overlaps with the phenolic acetoxyl proton of an acetylated sample in the original sample

Aar: An integrated value for an area indicating an aromatic proton signal (7.80-6.30 ppm) in the acetylated sample

Oar: An integrated value for an area indicating an aromatic proton signal (7.80-6.30 ppm) in the original sample

Aali: An integrated value for an area indicating an aliphatic acetoxyl proton signal (corrected value)

Aali': An integrated value for an area indicating an aliphatic acetoxyl proton signal (2.03-1.60 ppm) in the acetylated sample

Oali: An integrated value for an area (2.03-1.60 ppm) that overlaps with the phenolic acetoxyl proton of the acetylated sample in the original sample

[0114] The amount of hydroxyl group was calculated based upon these corrected values:

$$\text{phOHwt\%} = (\text{Pwt}/\text{Pm} \times \text{Pn}/\text{Pi} \times \text{Aph}/\text{An} \times \text{OHm}) / [\text{ALwt} - \{\text{Pwt}/\text{Pm} \times \text{Pn}/\text{Pi} \times (\text{Aph} + \text{Aali})/\text{An} \times \text{Acm} - 1\}] \times 100$$

$$\text{aliOHwt\%} = (\text{Pwt}/\text{Pm} \times \text{Pn}/\text{Pi} \times \text{Aali}/\text{An} \times \text{OHm}) / [\text{ALwt} - \{\text{Pwt}/\text{Pm} \times \text{Pn}/\text{Pi} \times (\text{Aali} + \text{Aph})/\text{An} \times \text{Acm} - 1\}] \times 100$$

$$\text{phOHmol/C9} = (\text{phOHwt\%}/\text{OHm}) / \{(100 - \text{Iwt\%})/\text{Lm}\}$$

$$\text{aliOHmol/C9} = (\text{aliOHwt\%}/\text{OHm}) / \{(100 - \text{Iwt\%})/\text{Lm}\}$$

phOHwt%: the amount of a phenolic hydroxyl group (wt%)

Pwt: Weight of PNB (mg)

Pm: Molecular weight of PNB (151)

Pn: Number of aromatic ring Hs in PNB (4)

Pi: Integrated value for an area indicating an aromatic ring 4H signal (8.40-7.80 ppm) in PNB

Aph: Integrated value for an area showing a signal of phenolic acetoxyl proton (corrected value)

An: Proton number of a methyl group in an acetoxyl group (3)

OHm: Mass number of a hydroxyl group (17)

ALwt: Weight of acetylated lignin (mg)

Aali: Integrated value for an area showing a signal of aliphatic acetoxyl proton (corrected value)

Acm: Mass number of an acetoxyl group (43)

phOHmol/C9: Amount of phenolic hydroxyl group (mol/C9)

Iwt%: Amount of introduced cresol (wt%)

Lm: Molecular weight of 1 unit of lignin (200)

aliOHwt%: Amount of an aliphatic hydroxyl group (wt%)

aliOHmol/C9: Amount of an aliphatic hydroxyl group (mol/C9)

3. Quantification of a hydroxymethyl group of a lignin cross-linking derivative

[0115] An example is explained below in which formaldehyde was used as a cross-linking functional group forming compound and a hydroxymethyl group was introduced as a cross-linking functional group. Also in the case where the other functional group was introduced, a structure can be determined similarly. Formaldehyde was calculated according to the following equation on the assumption that formaldehyde is all introduced as a hydroxymethyl group.

$$\text{HMwt\%} : \text{Weight of hydroxymethyl (wt\%)}$$

Pwt :Weight of PNB (mg)

Pm: Molecular weight of PMB (151)

Pn :Number of aromatic ring H in PNB (4)

Pi: Integrated value for an area showing an aromatic ring 4H signal (8.40-7.80 ppm) in PNB

Mi: Integrated value for an area showing a methylene signal (-CH₂-OAc) in a hydroxymethyl group (5.20-4.70 ppm)

Mn : Proton number of a hydroxymethyl group (2)

HMm: Mass number of a hydroxymethyl group (31)

Aph: Integrated value for an area showing a signal of phenolic acetoxyl proton (corrected value)

Aali: Integrated value for an area showing a signal of aliphatic acetoxyl proton (corrected value)

An: Proton number of a methyl group in an acetoxyl group (3)

ALwt: Weight of acetylated lignin (mg)

Acm: Mass number of an acetoxyl group (43)

HMmol/C9: Amount of a hydroxymethyl group (mol/C9)

lwt%: Amount of introduced cresol (wt%)

Lm: Molecular weight of 1 unit of lignin (200)

$$HMwt\% = (Pwt/Pm \times Pn/Pi \times Mi/Mn \times HMm) / [ALwt - \{Pwt/Pm \times Pn/Pi \times (Aph + Aali)/An \times (Acm - 1)\}] \times 100$$

$$HMmol/C9 = (HMwt\%/HMm) / \{(100 - (lwt\% + HMwt\%))/Lm\}$$

4. Average molecular weight

[0116] Measurement of average molecular weight in a lignophenol derivative, an arylcoumaran derivative and a lignin cross-linking derivative was performed by gel permeation chromatography. A sample for measurement was prepared by placing about 2 ml of distilled and degassed tetrahydrofuran (THF) (manufactured by Wako Pure Chemical Industries, Ltd., extra pure reagent) and each 1 mg of derivative in a test tube, stirring with a touch mixer to dissolve completely, adding one droplet of an about 4% p-cresol solution in THF as an internal standard substance to make completely uniform and filtering with a COSMONICE Filter "S". The measuring conditions were as follows:

Column: Shodex KF802 and KF804

Solvent: THF

Flow rate: 1 ml/min.

Detector: UV (280nm)

Range: 0.32

Amount of sample: 50 µl

[0117] A calibration curve was made using a Polystyrene standard (Mw: 390000, 233000, 100000, 25000, 9000, 4000, 2200, 760); bisphenol A and p-cresol provided that molecular weight of polystyrene was multiplied by a ratio of Q factor (0.5327) taking the molecular form of a hybrid derivative and an arylcoumaran derivative as well as polystyrene into consideration. The weight-average molecular weight (Mw), number-average molecular weight (Mn) of each sample were calculated according to the following equations and a variance ratio (Mw/Mn) was also calculated.

$$Mw = \sum (Hi \times Mi) / \sum Hi$$

$$Mn = \sum Hi / \sum (Hi/Mi)$$

wherein Hi is the Height of chromatogram read every 0.5 ml

Mi: Molecular weight read from the calibration curve every 0.5 ml

(Material for molded product other than the arylcoumaran derivative and the lignin cross-linking derivative)

[0118] As molding materials that are used for manufacturing molded products of the present invention, natural or synthetic fibrous, chip-like or powdery materials are used as molding substrate materials in addition to these lignin derivatives. The form of the molding substrate material is not limited to these forms and various forms can be widely used.

[0119] As fibrous molding substrate materials, various fibers such as natural or synthetic various hydrocarbon fibers, metal fibers, glass fibers, ceramic fibers, and fibers recycled from these fibers can be used.

[0120] Among others, cellulose fibers are preferable because they are readily available and reproducible. As the cellulose fiber, mechanical pulp, chemical pulp, semichemical pulp and pulps recycled from these pulps, as well as various artificial cellulose fibers synthesized using these pulps as a raw material can be used.

[0121] As a raw material for such the cellulose fiber, either timber fiber using a coniferous tree and a broadleaf tree as a raw material, or non-timber fiber such as paper mulberry, kenaf, Manila hemp, straw and bagasse can be utilized.

[0122] In addition, cellulose fibers obtained by splitting various products such as boards, newspapers and the like, which are pulp processed products manufactured from a lignocellulose material, also may be used.

[0123] As chip-like molding substrate materials, various materials such as natural or synthetic various hydrocarbon, metal, glass, ceramic and the like can be used. As hydrocarbon chips, natural cellulose chips from timber or non-timber materials may be used. As metal chips, alumina chips may be used. As ceramic chips, chips such as Al_2O_3 , SiO_2 and the like may be used. From the same reason as that for fibrous molding substrate materials, cellulose chips are preferable.

[0124] As powdery molding substrate materials, a molding material which is made into a powder by grinding or is originally in powder form and which is derived from the same material as that for the aforementioned chip material can be used.

(Preparation of a molded product using an arylcoumaran derivative and/or a lignin cross-linking derivative)

[0125] In order to prepare a molded product, only an arylcoumaran derivative can be used, or only a lignin cross-linking derivative can be used, or both the arylcoumaran derivative and the lignin cross-linking derivative can be used.

[0126] In order to prepare a molded product using an arylcoumaran derivative and/or a lignin cross-linking derivative (hereinafter referred to as secondary derivative or the like), a secondary derivative or the like, which is in melted state or a solvent dissolved state (hereinafter this state is referred to as liquefied state), is added to a molding substrate material and a secondary derivative or the like in this liquefied state and is solidified.

[0127] The secondary derivative or the like exhibits caking properties when it changes from the liquefied state into a solid. That is, when it precipitates into a solid by distilling the solvent off from the liquefied state, or when it solidifies from a melted state by cooling, the adhesive properties and the caking properties are exhibited. By utilizing such a caking property exhibiting process, the secondary derivative or the like can be used as a binder for mutually adhering molding substrate materials.

[0128] Therefore, upon preparation of the molded product, the secondary derivative or the like is usually passed through a process in which a secondary derivative or the like in a solution state is added to the molding material and is liquefied and thereafter, the solvent is distilled off, or a process in which a secondary derivative or the like in the solid state is added, heated to melt and liquefy and then cooled.

[0129] The secondary derivative or the like solution used herein is a liquid in the state in which the secondary derivative or the like is dissolved in a solvent. As a solvent used for this derivative solution, acetone, ethanol, methanol, dioxane, tetrahydrofuran, or a mixture of each of them with water can be used. In addition, a secondary derivative or the like solution obtained in a step for synthesizing and separating a secondary derivative or the like from a lignocellulose material may be also used.

[0130] For example, as a method for preparing a molded product, a method comprising steps shown FIGS. 27 to 31 is provided.

[0131] As shown in FIG. 27, a cellulose fiber is molded, and this molded product is impregnated with a secondary derivative or the like solution and a solvent is distilled off. By removal of a solvent by distillation, the secondary derivative or the like provides caking properties and adhesive properties to molding materials. As a result, the secondary derivative or the like is attached to the cellulose fiber to obtain a molded product in the state in which the secondary derivative or the like acts as a binder. If needed, this molded product may be further molded by pressurizing and/or heating.

[0132] Alternatively, as shown in FIG. 28, a cellulose fiber is molded, and the molded product is impregnated with a secondary derivative or the like solution. Thereafter, the solvent is distilled off by pressurizing and/or simultaneously heating this molded product. By removal of the solvent by distillation, a secondary derivative or the like provides caking properties and adhesive properties to molding materials. As a result, a lignophenol molded product in the state in which a secondary derivative or the like acts as a binder can be obtained.

[0133] According to methods shown in FIGS. 27 and 28, a secondary derivative or the like is transferred to the surface layer side in the solvent distillation step. FIG. 29 shows transference to the surface layer exemplified with an arylcoumaran derivative. That is, a large amount of secondary derivative or the like is attached to the surface layer of the molded product. Therefore, because a large amount of secondary derivative or the like is present on the surface layer side by attaching a relatively small amount of the secondary derivative or the like, a molded product having water-resistance and strength can be obtained by the binding action of the secondary derivative or the like on the surface layer side.

[0134] In this case, particularly when a highly hydrophobic arylcoumaran is used, i.e., an arylcoumaran derivative synthesized from a lignophenol derivative with cresol, a highly hydrophobic molded product can be efficiently obtained.

[0135] Further, as shown in FIG. 30, after cellulose fiber in the unmolded state is impregnated with the secondary derivative or the like, the solvent is distilled off. Thereafter, this fiber is molded by heating and/or pressurizing.

[0136] According to this method, a secondary derivative or the like is attached to a fiber in advance using the adhesive properties by distilling the solvent off. As such, by molding with heating and pressurization using a fiber to which a secondary derivative or the like is attached in the solid state in advance, a molded product in which a secondary derivative or the like is uniformly distributed throughout the product can be molded via from the liquid state to the solid state. Therefore, this method is preferable as a process for preparing a molded product having uniform properties.

[0137] Further, as shown in FIG. 31, a powdery secondary derivative or the like is mixed into a cellulose fiber and molded by heating and/or pressurizing. Alternatively, prior to the final molding, a provisional molding step can be performed by pressurizing. Thereafter, such provisionally molded product is heated to mold and, if necessary, pressurized. According to this method, the solvent distillation step becomes unnecessary. In addition, a molded product in which a secondary derivative or the like is uniformly distributed throughout the product can be formed and thus, a molded product having uniform physical properties can be manufactured.

[0138] In addition, upon preparation of the molded product from various molding materials and a secondary derivative or the like, provisional molding before molding or a molding method can be variously selected and added and further other additional steps may be added. For example, when a fibrous pulp is used as the molding material, a wet process or a dry process for forming a molded product and a provisional molding method and the like may be used and are different processes.

(Preparation of a molding product using a lignin cross-linking derivative)

[0139] In a molded product using a lignin cross-linking derivative, the molding substrate can be strengthened by cross-linking and heating the molding substrate material to which the linking cross-linking derivative is attached. Heating may be accompanied with pressurizing. Formation of cross-links is also possible by heating when distilling the solvent off from the molding substrate material to which a cross-linking derivative in the liquid state is attached.

[0140] In the case of a molded product in which cross-linking of a cross-linking derivative was performed, the hydrophobicity is improved and, in particular, the strength is improved.

(Recovery of an arylcoumaran derivative from an molded product)

[0141] Further, as shown in FIG. 32, by adding again a solvent to the present molded product, the product can be separated into fibers and an arylcoumaran derivative, which can be recovered.

[0142] The arylcoumaran derivative is extracted from the molded product using a solvent having affinity for the arylcoumaran derivative (hereinafter referred to as the present solvent).

[0143] In this case, the present solvent may be acetone, ethanol, methanol, dioxane, tetrahydrofuran, a mixture of one of these solvents and water, or an aqueous alkali solution and the like. Considering simplicity, acetone and alcohol are preferable. In addition, considering the cost, an aqueous alkali solution is preferable.

[0144] More particularly, during the recovery of the arylcoumaran derivative, whether the original shape of the molded product is maintained or the molded product is processed into small pieces, the molded product or the small pieces are dipped into a solvent having affinity for the arylcoumaran derivative and further stirred. As a result, the arylcoumaran derivative is extracted into the solvent. By processing the molded product into small pieces and stirring into the solvent, rapid separation and extraction become possible. Alternatively, when the original shape of the molded product is desired to be maintained, the arylcoumaran derivative is dipped into a solvent having affinity for the arylcoumaran derivative, but the solvent is non-aqueous (for example, acetone) and allowed to stand to extract without stirring. In particular, in the case of a molding substrate material using a cellulose system, when the arylcoumaran derivative is intended to be extracted and, at the same time, the molded product is intended to be separated into molding materials by splitting or the like, the molded product is dipped into an aqueous alkali solution and stirred.

[0145] As such, the recovered arylcoumaran derivative can be utilized again in various fields in addition to preparation of molded products. In addition, molding substrate materials that were separated at the same time can be utilized again in various fields in addition to preparation of molded products.

(Recovery of a lignin cross-linking derivative from a molded product)

[0146] In addition, when the molded product is prepared by heating without cross-linking, the lignin cross-linking derivative can be recovered from the molded product using a solvent having affinity for the lignin cross-linking derivative, as was the case for the arylcoumaran derivative. Solvent having affinity for the lignin cross-linking derivative are

acetone, ethanol, methanol, dioxane, tetrahydrofuran, a mixture of one of these solvents and water, or an aqueous alkali solution and the like. Considering simplicity, acetone and alcohol are preferable. In addition, considering the cost, an aqueous alkali solution is preferable.

[0147] According to the present invention, a lignophenol derivative is obtained from various lignocellulose materials via a phase separating process with a phenol derivative and concentrated acid and this derivative is further secondarily-derivatized to obtain an arylcoumaran derivative or a lignin cross-linking derivative that can be complexed with various fibers to prepare a molded product. The derivative and the fiber material in the molded product are separated from the molded product. Therefore, by using an arylcoumaran derivative and a cross-linking derivative as a material for molding, preparation of the molded product and separation can be repeatedly performed. Therefore, a lignocellulose can be efficiently reused.

[0148] Arylcoumaran derivatives produced according to the present invention can be used as an ultraviolet absorber or a lignin material having low protein absorbing properties.

[0149] Lignin cross-linking derivatives produced according to the present invention can be used as a switching element, a hydrophilic high protein absorber, an ultraviolet absorber or the like.

Examples

[0150] The following Examples illustrate the present invention. In the following Examples, preparation of a molded product of a cellulose fiber using an arylcoumaran derivative and a lignin cross-linking derivative, and recovery of each derivative from a molded product are explained. The steps of Examples 1 to 3 are shown in FIG. 33.

(Example 1)

(Synthesis of a lignophenol derivative)

[0151] Lignocresol as a lignophenol derivative was synthesized using *Pinus Thunbergii* as the lignocellulose material according to the following steps. That is, to *Pinus Thunbergii* defatted wood powder was added an acetone solution containing about 3 mole-amounts per lignin C₉ unit in the *Pinus Thunbergii* defatted wood powder and the mixture was well stirred and allowed to stand overnight to impregnate the wood powder with p-cresol. Thereafter, the wood powder was thinly spread in a vat and allowed to stand in a draft until the acetone odor is lost due to distillation of the acetone. The amount of C₉ unit in the lignin in the *Pinus Thunbergii* defatted wood powder was calculated based on elementary analysis of the lignin in the *Pinus Thunbergii* defatted wood powder.

[0152] Then, 250 g of wood powder with p-cresol adsorbed thereon was placed into a beaker, and 1200 ml of 72% sulfuric acid was added thereto while stirring with a glass bar. After stirred for about 10 minutes, the mixture was further stirred with a stirrer for 1 hour and thereafter, the reaction was stopped by the addition of 10 L of water. After allowing it to stand for a few days, the precipitate fraction was deacidified by dialysis. After the precipitate was dried in a drier at 40°C for a few days, the lignophenol derivative fraction was extracted with acetone, the acetone fraction was added dropwise to a large excess of benzene : hexane (2:1) (v/v) while stirring, and the produced precipitate was washed with ethyl ether. Afterwards, the precipitate was dried at room temperature and atmospheric pressure, and dried over phosphorus pentoxide under reduced pressure to obtain the lignophenol derivative (lignocresol).

[0153] The molecular weight, the amount of introduced cresol, the hydroxyl group distribution and the phenolic property frequency of this lignophenol derivative are shown in FIGS. 34 and 35.

(Example 2: Synthesis of an arylcoumaran derivative)

[0154] 4 g of the lignophenol derivative obtained in Example 1 was dissolved in 80 ml of a 0.5N aqueous sodium hydroxide solution, was placed into a stainless steel autoclave and heated at 140°C for 6 hours and allowed to react. The reaction was stopped by cooling, acidified to pH 2 with 1N hydrochloric acid, the produced precipitate was collected by centrifuging, and washed to neutral. The resulting precipitate was lyophilized and dried over phosphorus pentoxide under reduced pressure to obtain an arylcoumaran derivative. The molecular weight, the amount of introduced cresol, the hydroxyl group distribution and phenolic property frequency are shown in FIGS. 34 and 35.

(Example 3: Synthesis of a lignin cross-linking derivative)

[0155] Lignocresol was obtained according to the same method as that of Example 1. The molecular weight and the amount of introduced cresol of this lignocresol are shown in FIG. 36.

[0156] 20 g of this lignophenol derivative was placed into three-necked flask, was dissolved with 1.2 L of a 0.1N aqueous sodium hydroxide solution, and 180 ml of a 37% formaldehyde solution (corresponding to 20 mole-amount of

formaldehyde relative to introduced cresol and the main lignin structure aromatic ring) was added, heated at 60°C for 3 hours to introduce the cross-linking functional group. The reaction was stopped by cooling, acidified to pH 2 with 5% hydrochloric acid and the whole solution was transferred into a dialysis membrane, where the acid and unreacted formaldehyde were removed. After dialysis, a sample was recovered by lyophilizing and dried over phosphorus pentoxide under reduced pressure to obtain the lignin cross-linking derivative. The molecular weight and the amount of introduced cresol of this lignin cross-linking derivative are shown in FIG. 36. In addition, the hydroxyl group distribution and the amount of hydroxymethyl thereof are shown in FIG. 37.

(Example 4: Attachment of various derivatives to a cellulose fiber mat)

[0157] Regenerated paper was used as the cellulose material, was dipped into water overnight, splitted well and thereafter, fibers were aggregated using a cylinder having a diameter of about 10 cm. Then, the aggregate was dehydrated and dried to prepare a mat having a diameter of about 100 mm and a thickness of 9 mm.

[0158] A mat piece A, 20 mm × 90 mm, for preparing sample for the strength test, and a mat piece B, 20 × 20 mm, for preparing a sample for the water absorbing test were cut and taken from this fiber mat using a motor disc saw.

(1) Preparation of a mat for the strength test

[0159] The lignophenol derivative obtained in Example 1 or the arylcoumaran derivative obtained in Example 2 was attached to this mat piece A at a ratio of 5%, 10% or 20% by weight. In addition, the lignin cross-linking derivative was attached to a mat piece A at a rate of 15% by weight. That is, the aforementioned lignophenol derivative, the arylcoumaran derivative or the lignin cross-linking derivative was dissolved in acetone separately to prepare a solution for attachment, and a predetermined amount of the aforementioned solution for attachment was added separately so that the lignophenol derivative or the arylcoumaran derivative was attached to various mat pieces at a rate of 5%, 10% or 20%, respectively, in a cylindrical stainless steel container having a diameter of 10 cm. The lignin cross-linking derivative obtained in Example 3 was attached to mat piece A at a ratio of 15%, which was dipped in the solution overnight to allow the solution to thoroughly permeate for attachment into mat piece A. Thereafter, acetone was gradually evaporated while turning over mat piece A every 1 hour, to attach various derivatives to mat piece A.

[0160] Mat piece A was removed from the container at the point in time when the acetone appeared to completely evaporated from the container based upon visual observation, the remaining acetone in the interior of the mat was evaporated in a blast drier at 60°C, and the weight was measured. The initial weight of a mat was subtracted from the weight after attachment of the derivative to calculate the amounts of various derivatives.

[0161] With regard to mat piece A having an attached cross-linking derivative, after the cross-linking derivative was attached thereto, heating treatment was performed at 170°C for 60 minutes to prepare a heat-treated material.

(2) Preparation of a mat for the water absorbing test

[0162] The lignophenol derivative obtained in Example 1 or the arylcoumaran derivative obtained in Example 2 was attached to mat piece B at a ratio of 5%, 10% or 20% by weight, respectively, similar to the mat for the strength test. In addition, a lignin cross-linking derivative was attached to a mat piece B at a ratio of 20% by weight, similar to the mat for the strength test.

[0163] Moreover, mat pieces B with various derivatives attached were heated at 170°C for 60 minutes to prepare heat-treated materials, respectively (only heat-treated material was prepared for the mat piece having the attached lignin cross-linking derivative).

[0164] For comparison in assessment described below, a control mat piece with nothing attached thereto was made according to the same steps as those of this Example, except for the attaching step. Also regarding the control mat piece, a heat-treated compound was prepared by heating at 170°C for 60 minutes.

(Example 5: Assessment)

[0165] Various mats thus prepared were tested for the following items.

(Appearance)

[0166] The various mat pieces were observed with the naked eye.

[0167] The various mat pieces turned brown as a whole, and heat-treated materials made by heat-treating the mat pieces were all uniformly and densely colored.

(Mat strength test)

[0168] Mat piece A for the strength test and the control mat piece were tested using a span length of 80 mm and using the steel apparatus shown in FIG. 38 for supporting the test piece and providing a load. A concentrated load was applied to the entire width of a span center from the surface of the test piece and the average load rate was 2 mm/min.

[0169] According to this test apparatus and method, a load-deflection curve was prepared and, from this curve, modulus of elasticity (MOE) and modulus of rupture in bending (MOR) were calculated. In addition, Pmax was calculated.

[0170] The results are shown in FIGS. 39 (a), 39 (b) and 39 (c).

[0171] From the results of FIGS. 39 (a), 39 (b) and 39 (c), the arylcoumaran derivative was excellent for each of Pmax, modulus of elasticity and modulus of rupture in bending as compared with the lignophenol derivative. Therefore, it was seen that the molded product with the arylcoumaran derivative attached thereto has the increased strength as compared with the corresponding molded product using the lignophenol derivative. In addition, it was seen that the arylcoumaran derivative has improved function as a binder, even when it was obtained by low-molecularizing the lignophenol derivative.

[0172] Moreover, the molded product (heat-treated material) using the cross-linking derivative had a much greater Pmax, modulus of elasticity and modulus of rupture in bending than those of the arylcoumaran derivative and it was seen that the strength can be greatly improved.

(Water absorbing test)

[0173] A stainless steel net was placed on the bottom of a vat, water was added so that the distance from the net bottom to the surface of water was 3 cm and the temperature of water was maintained at 25°C. Mat piece B prepared for the water absorbing test was immersed therein and a stainless steel net as a weight was placed on the upper surface of mat piece B and allowed to stand for 1 hour in order to maintain the upper surface of test piece B at 3 cm under the surface of the water, so as not to float.

[0174] After a predetermined period of time, the immersed mat piece B was taken out, placed on a stainless steel net and after 10 minutes, the test piece was rapidly rolled onto a filter to remove water droplets on the surface thereof, the weight and dimensions were measured and a volumetric change rate relative to before immersion in water was calculated. The results thereof are shown in FIGS. 40 to 42.

[0175] In addition, mat piece B after immersion in water was allowed to stand at 105°C for 15 hours in a drier, removed, cooled, and the weight and dimensions thereof were measured. A volumetric change rate of mat piece B after drying was calculated and compared with the volumetric change rate after immersion in water in order to assess the dimensional stability of the molded product. The results are also shown in FIGS. 40 to 43.

[0176] As is apparent from the results of FIG. 40, the unheated material of the heat-treated material of mat pieces B with a lignophenol derivative attached thereto at various amounts displayed a volumetric change rate of about 5 to 10% and after drying, had a volumetric change rate of about 3 to 2%.

[0177] To the contrary, mat pieces B with an arylcoumaran derivative attached thereto (unheated material and heat-treated material) had a volumetric change rate of about 7 to 10% and after drying, had about -1 to 1%. That is, although the volumetric change rate after immersion in water was similar to that of the molded product with the lignophenol derivative attached thereto and there was no great difference, after re-drying, the volume was as great as that before immersion in water (see FIG. 41). Therefore, the dimensional stability of a mat piece B with an arylcoumaran derivative attached thereto can be said to be better. In addition, the amount of water absorption was almost same as that of the lignophenol derivative.

[0178] In addition, although mat piece B with the cross-linking derivative attached thereto had a volumetric change rate of about 7% after immersion in water, the volume returned back to nearly that before immersion in water after re-drying and thus, it was seen that mat piece B with the cross-linking derivative attached thereto had better dimensional stability. With respect to water absorption, mat piece B with the cross-linking derivative attached thereto had about 60% of the water absorption of that of the mat piece B with the arylcoumaran derivative attached thereto and that of mat piece B with the lignophenol derivative attached thereto; thus, it was seen that water-resistance was improved by cross-linking (see FIG. 42, in this figure, comparison was performed on a heated material of each derivative having an attached amount of 20%).

[0179] From these results, it was clear that by attaching the arylcoumaran derivative or the lignin cross-linking derivative obtained by further secondarily-derivatizing lignocresol to a molding substrate material, the water absorption of the mat was reduced. As a result, dimensional stability with respect to moisture was imparted thereto. In particular, this tendency was remarkable in mat piece B with the lignin cross-linking derivative attached thereto (heat-treated material).

(Example 6: Test for recovering lignocresol from a board)

[0180] Mat piece B for the water absorption test with each of a lignophenol derivative, an arylcoumaran derivative and a cross-linking derivative was prepared according to Example 4, and was used as a mat piece for the recovery test. With respect to the material with the lignophenol derivative attached thereto and the material with the arylcoumaran derivative attached thereto, a non-heated material and a heat-treated material (170°C, 60 min.) were prepared to obtain a mat piece for the recovery test and, with respect to the lignin cross-linking derivative, a heat-treated material (170°C, 60 min.) was used as the mat piece for the recovery test. The amount of each derivative to be attached was 20% by weight per weight of the cellulose fiber in every case.

[0181] These mats were immersed into about 30 ml of THF in a vial. Afterwards, they were allowed to stand for 2 days without stirring, the immersion solution was filtered, washed with THF, the filtrate and the washing solution were combined, THF was distilled off, and the resulting fraction was used as a recovery fraction. The results are shown in FIG. 44.

[0182] As apparent from the results of FIG. 44, 100% of the arylcoumaran derivative was recovered.

[0183] The better recovery rate is further effective in that the arylcoumaran derivative does also not remain on one side of the cellulose material. A trace of a lignin cross-linking derivative was recovered due to its cross-linked structure.

[0184] In addition, in the case of the lignophenol derivative and the arylcoumaran derivative, cellulose material was recovered in the reusable state.

[0185] As such, according to the first invention and the fourth invention, lignin that is a component of a lignocellulose complex structure of a forest resource can be efficiently utilized and a new functional material can be provided.

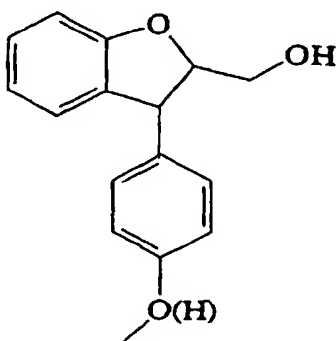
[0186] According to the fifth invention, a molded product can be provided that can be easily incorporated into a molding substrate material and can be again separated and reused together with a molding substrate and a binder material.

[0187] According to the sixth invention, a molded product can be provided that has water-resistance and strength.

[0188] According to the seventh invention, an arylcoumaran derivative can be efficiently and repeatedly utilized and a molding substrate material can be efficiently reused.

Claims

1. A process for producing a novel lignin derivative, which comprises using a lignophenol derivative containing a diphenylpropane unit formed by binding a carbon atom at an ortho-position relative to a phenolic hydroxyl group of a phenol derivative to a carbon atom at a benzyl-position of a phenylpropane fundamental unit of lignin, and binding an oxygen atom of the hydroxyl group and a β -positional carbon atom under alkali conditions under which the hydroxyl group can dissociate, to obtain an arylcoumaran derivative containing an arylcoumaran unit in which a coumaran skeleton is bound to an aromatic ring of a phenylpropane unit of lignin.
2. A novel lignin derivative represented by the following chemical formula and having an arylcoumaran unit in which a coumaran skeleton is bound to an aromatic ring of a phenylpropane unit of lignin.
Chemical formula:



3. A process for producing a novel lignin derivative, which comprises heating a lignophenol derivative containing a

5 diphenylpropane unit formed by binding an aromatic carbon atom of a phenol derivative to a carbon atom at a benzyl-position of a phenylpropane unit of lignin, with a cross-linking functional group forming compound under alkali conditions under which a phenolic hydroxyl group of an introduced phenol derivative and/or a phenolic hydroxyl group originally existing in lignin can dissociate, to introduce a cross-linking functional group at an ortho-position and/or para-position of the phenolic hydroxyl group to obtain a lignin cross-linking derivative containing a diphenylpropane unit having a cross-linking functional group.

- 10 4. A novel lignin derivative having a cross-linking functional group at an ortho-position and/or a para position relative to a phenolic hydroxyl group of a lignophenol derivative containing a diphenylpropane unit formed by binding an aromatic carbon atom of a phenol derivative to a carbon atom at a benzyl-position of a phenylpropane unit of lignin.
5. A molded product obtained by molding a fibrous, chip-like or powdery molding substrate material, which comprises the arylcoumaran derivative according to claim 3.
- 15 6. A molded product obtained by molding a fibrous, chip-like or powdered molding substrate material, which comprises the lignin cross-linking derivative according to claim 4.
7. A method for treating a molded product, which comprises adding a solvent having affinity for an arylcoumaran derivative to a molded product containing the arylcoumaran derivative and recovering the arylcoumaran derivative.

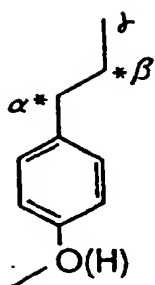


FIG.1

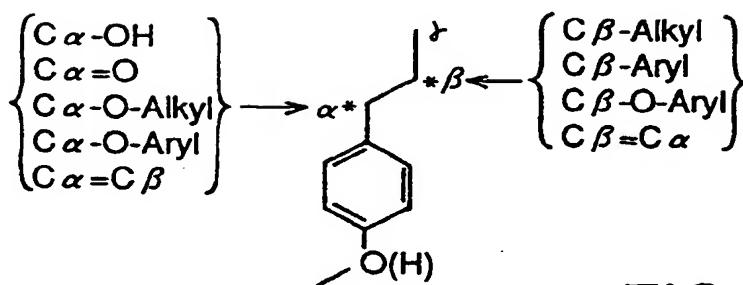


FIG.2

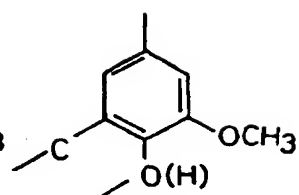
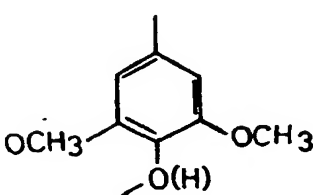
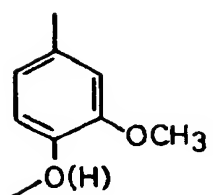
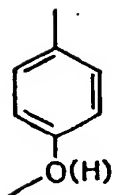


FIG.3 (a) FIG.3 (b) FIG.3 (c) FIG.3 (d)

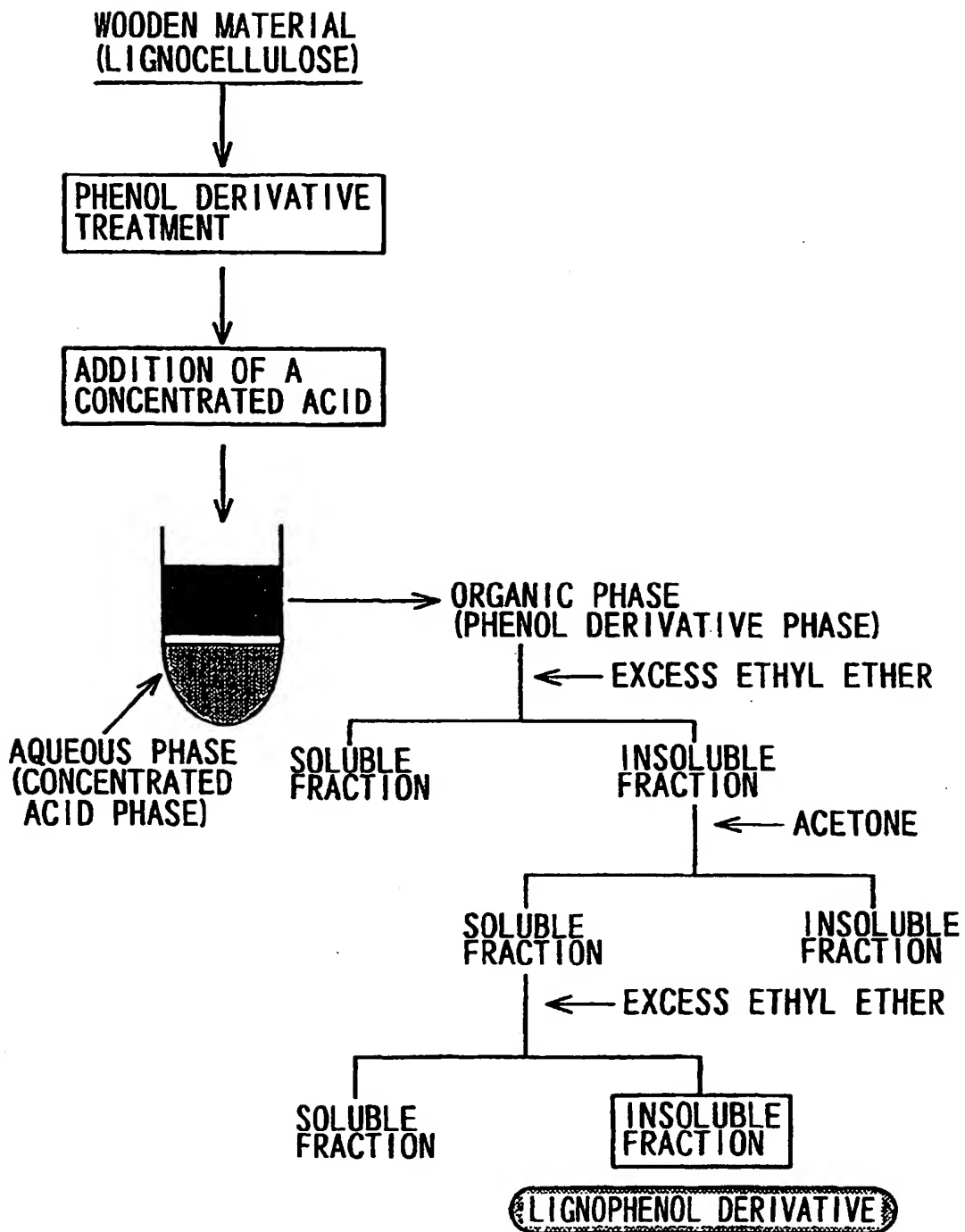


FIG.4

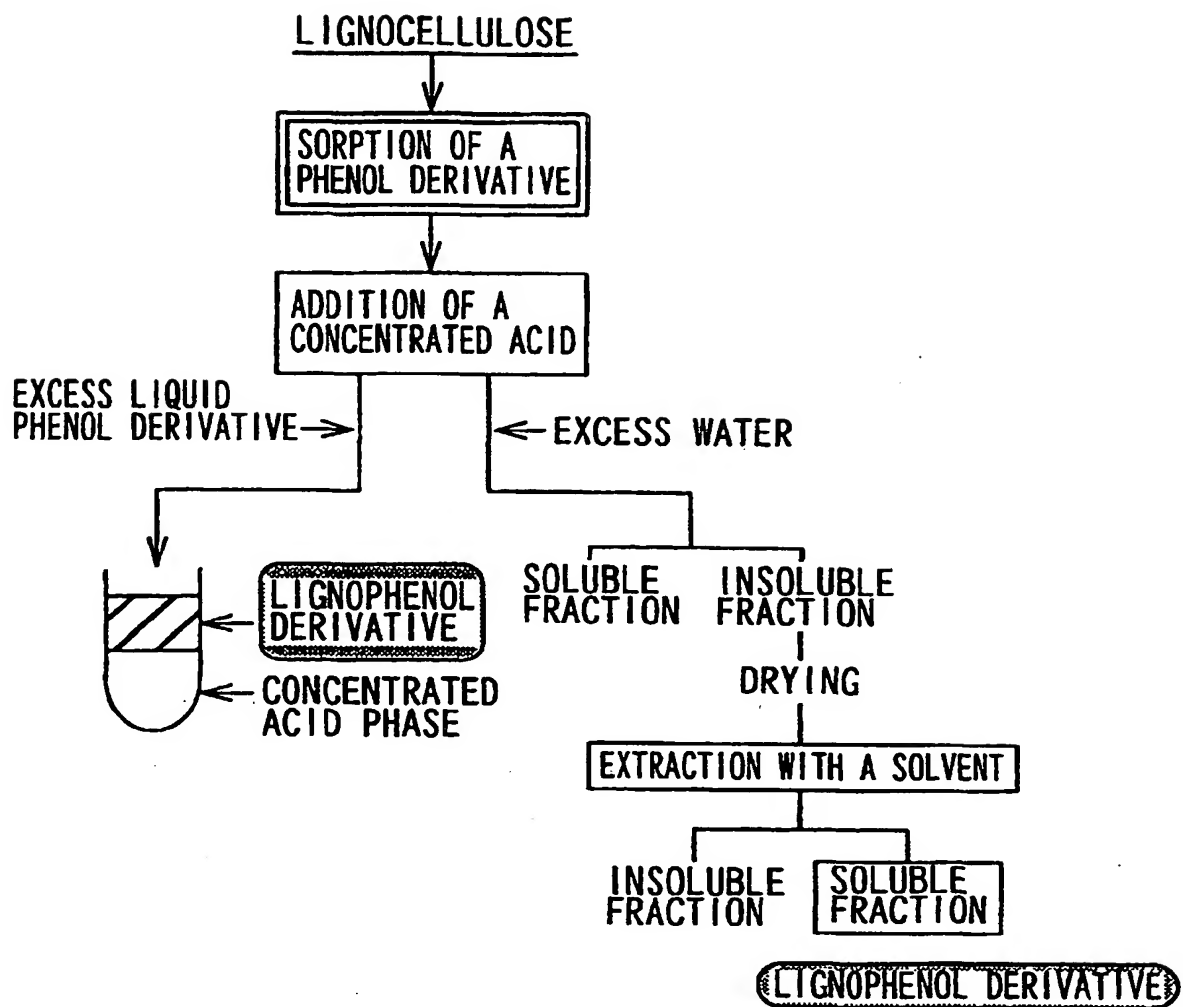


FIG.5

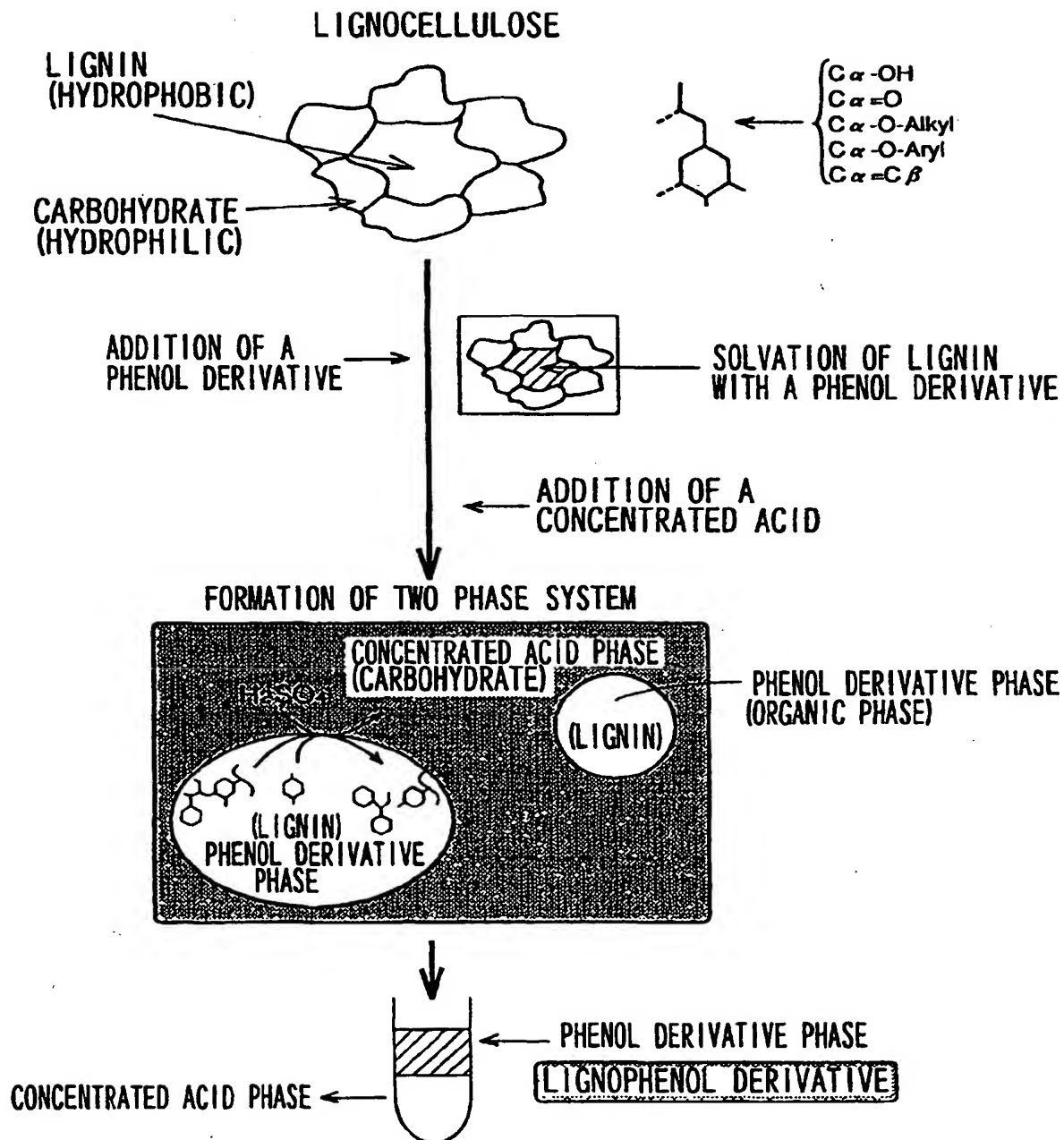


FIG.6

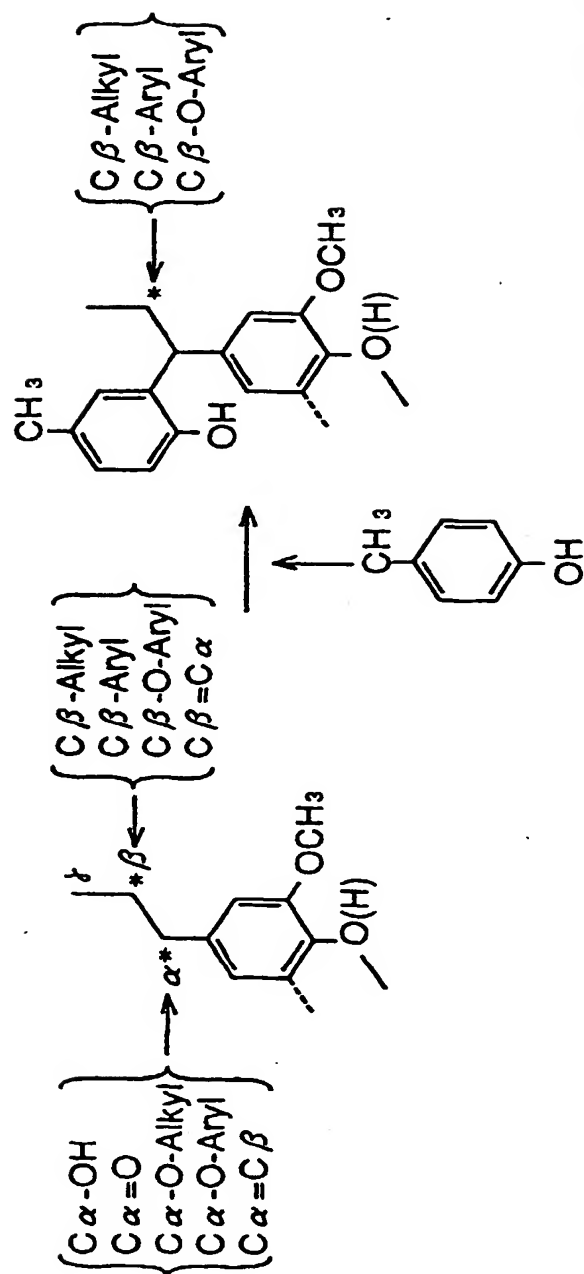


FIG.7

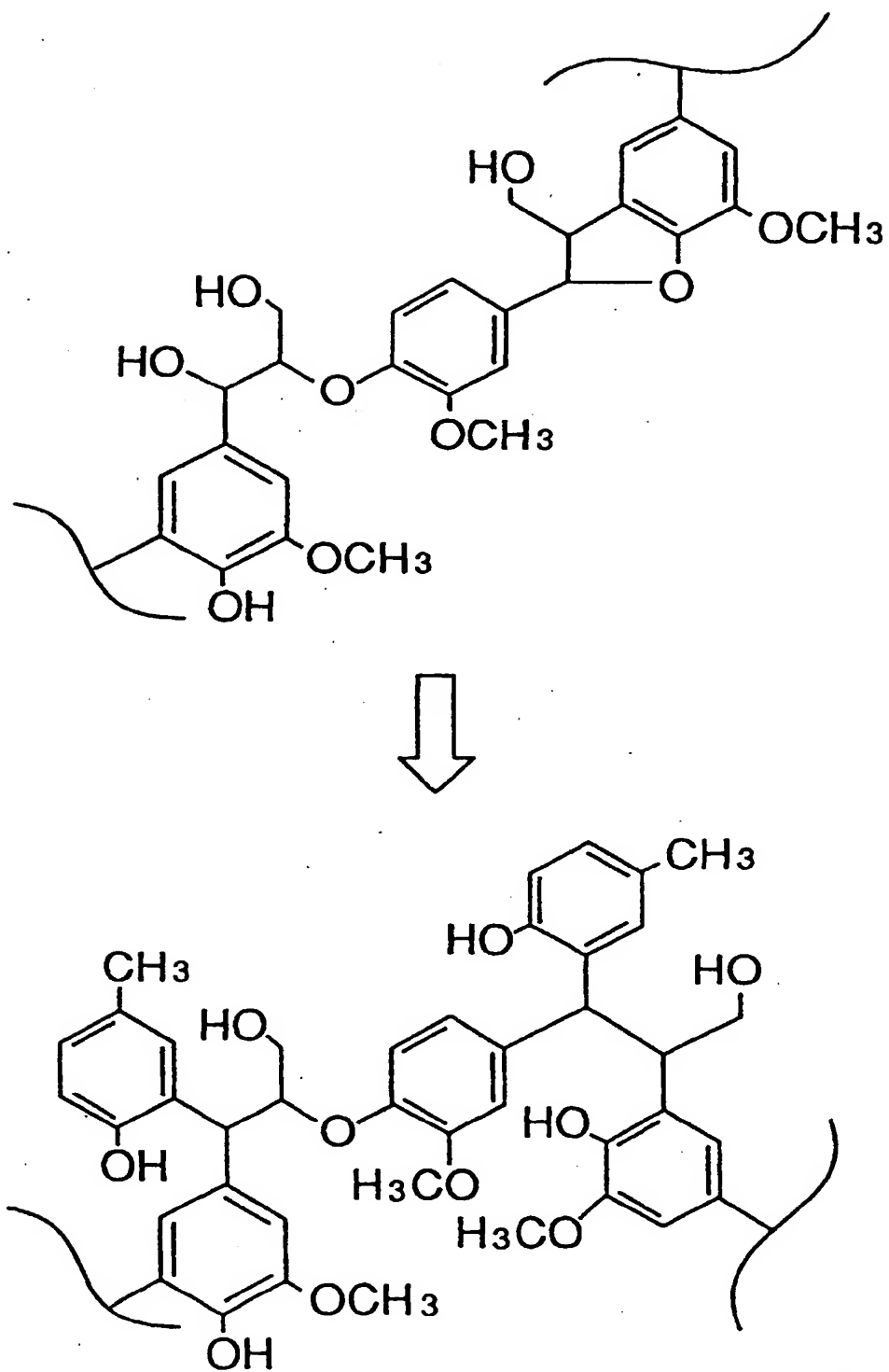


FIG.8

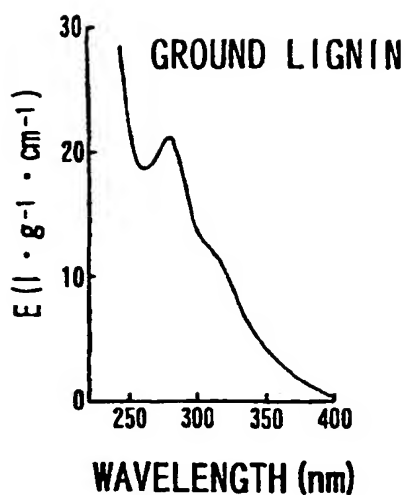


FIG.9 (a)

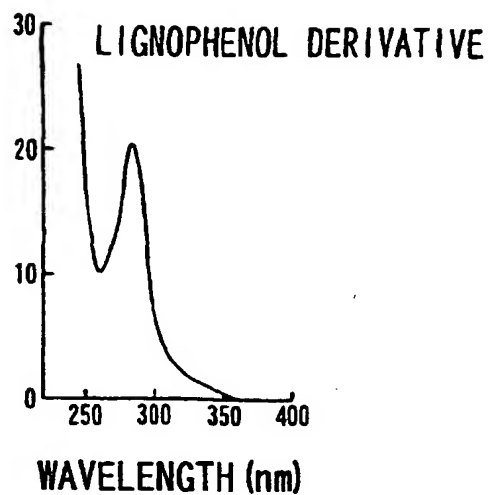


FIG.9 (b)

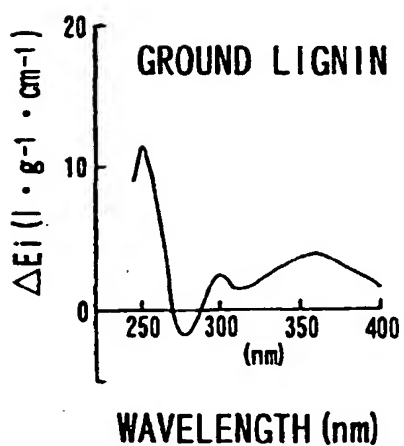


FIG.10 (a)

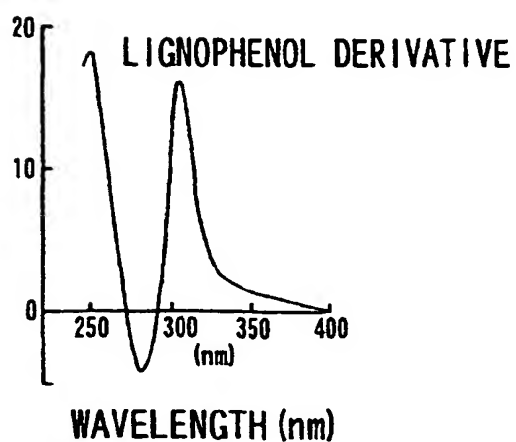
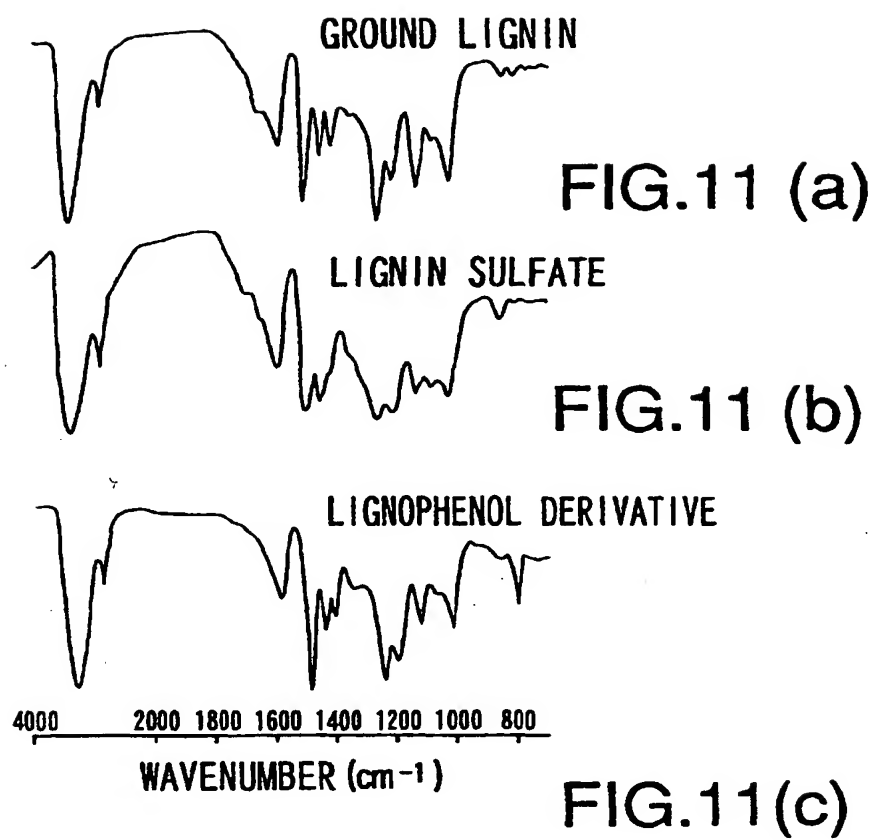


FIG.10 (b)



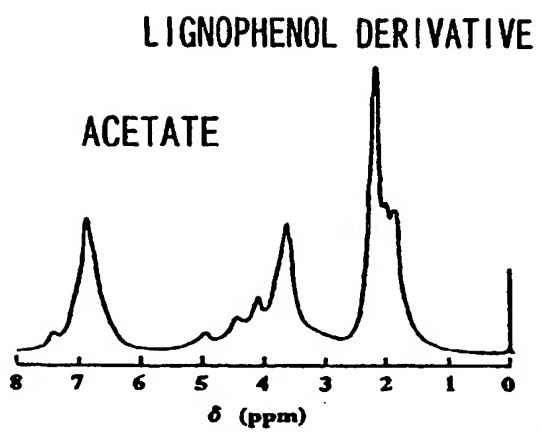


FIG.12 (a)

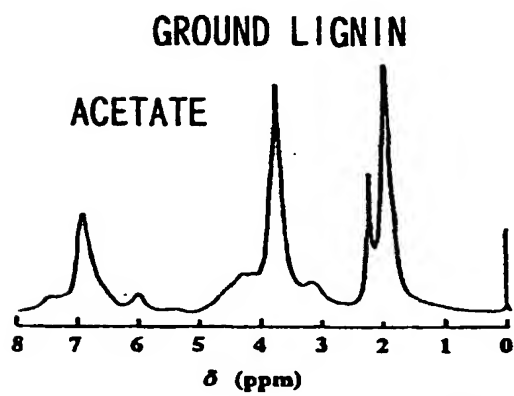


FIG.12 (b)

SAMPLE		YIELD (% of Klason lignin)
Yezo spruce	(<i>Picea jezoensis</i>)	108.2
Japanese fir	(<i>Abies firma</i>)	111.8
Japanese cedar	(<i>Cryptomeria japonica</i>)	110.3
Japanese birch	(<i>Betula platyphylla</i>)	103.0
Japanese oak	(<i>Quercus mongolica</i>)	109.3
Apitong	(<i>Dipterocarpus grandiflorus</i>)	101.6

FIG.13

SAMPLE	ELEMENTARY ANALYSIS RESULTS			INTRODUCED CRESOL		APPEARANCE	DISSOLVING SOLVENT
	C	H	O	%	mol/C ₉		
GROUND LIGNIN							
Yezo spruce (<i>Picea jezoensis</i>)	61.5	5.8	32.7				
LIGNOPHENOL DERIVATIVE							
Yezo spruce (<i>Picea jezoensis</i>)	66.8	6.0	27.2	25.9	0.65	Light pink	Methanol Ethanol Acetone Dioxane THF Pyridine DMF etc.
Japanese fir (<i>Abies firma</i>)	66.5	5.8	27.7	25.0	0.62		
Japanese cedar (<i>Cryptomeria japonica</i>)	66.2	5.9	27.9	24.8	0.62		
Japanese birch (<i>Betula platyphylla</i>)	59.7	6.1	34.2				
Japanese birch (<i>Betula platyphylla</i>)	64.3	6.0	29.7	30.9	0.90	Light pink	
Japanese oak (<i>Quercus mongolica</i>)	65.0	6.1	28.9	26.0	0.81		
Apitong (<i>Dipterocarpus grandiflorus</i>)	67.9	6.1	26.0	33.2	0.92		

FIG.14

SAMPLE	HYDROXYL GROUP (mol/C9)		
	C _α	C _γ	Phenolic
GROUND LIGNIN			
Yezo spruce (<i>Picea jezoensis</i>)	0.35	0.80	0.35
LIGNOPHENOL DERIVATIVE			
Yezo spruce (<i>Picea jezoensis</i>)	Trace	0.79	1.26
Japanese fir (<i>Abies firma</i>)	Trace	0.89	1.32
Japanese cedar (<i>Cryptomeria japonica</i>)	Trace	0.86	1.31
GROUND LIGNIN			
Japanese birch (<i>Betula platyphylla</i>)	0.53	0.82	0.32
LIGNOPHENOL DERIVATIVE			
Japanese birch (<i>Betula platyphylla</i>)	Trace	0.80	1.51
Japanese oak (<i>Quercus mongolica</i>)	Trace	0.88	1.51
Apitong (<i>Dipterocarpus grandiflorus</i>)	Trace	0.91	1.58

FIG.15

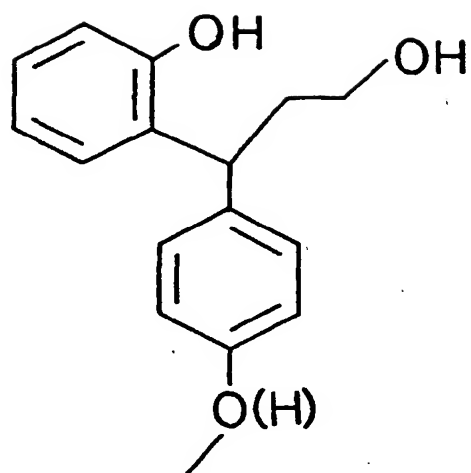


FIG.16

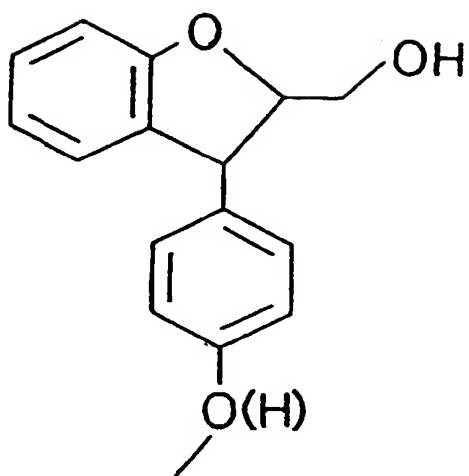


FIG.17

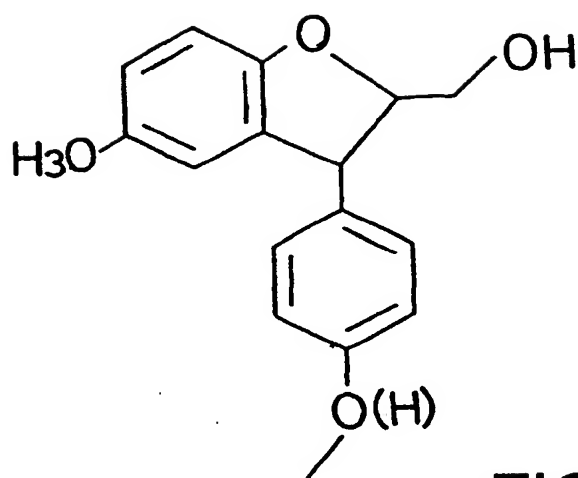


FIG.18

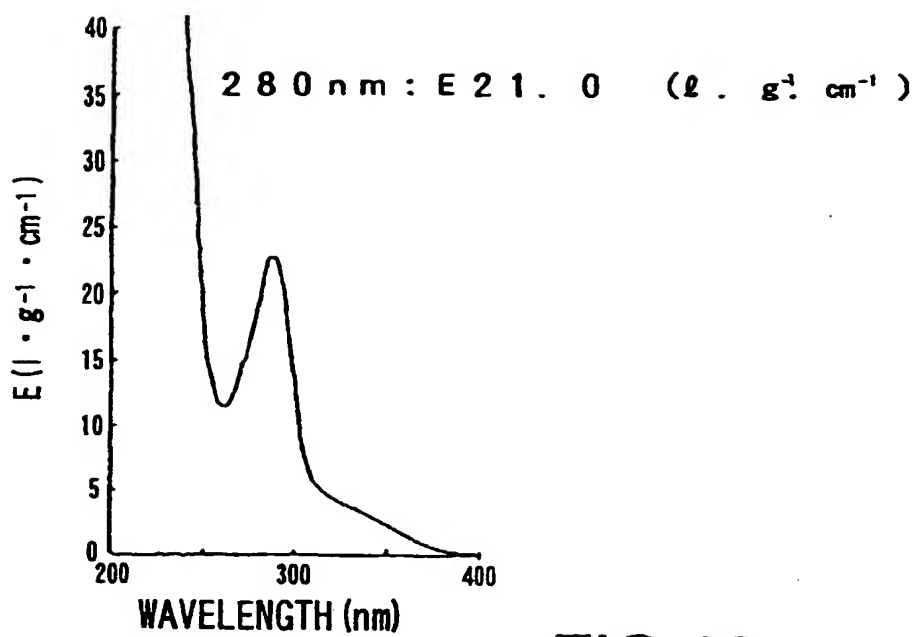


FIG.19

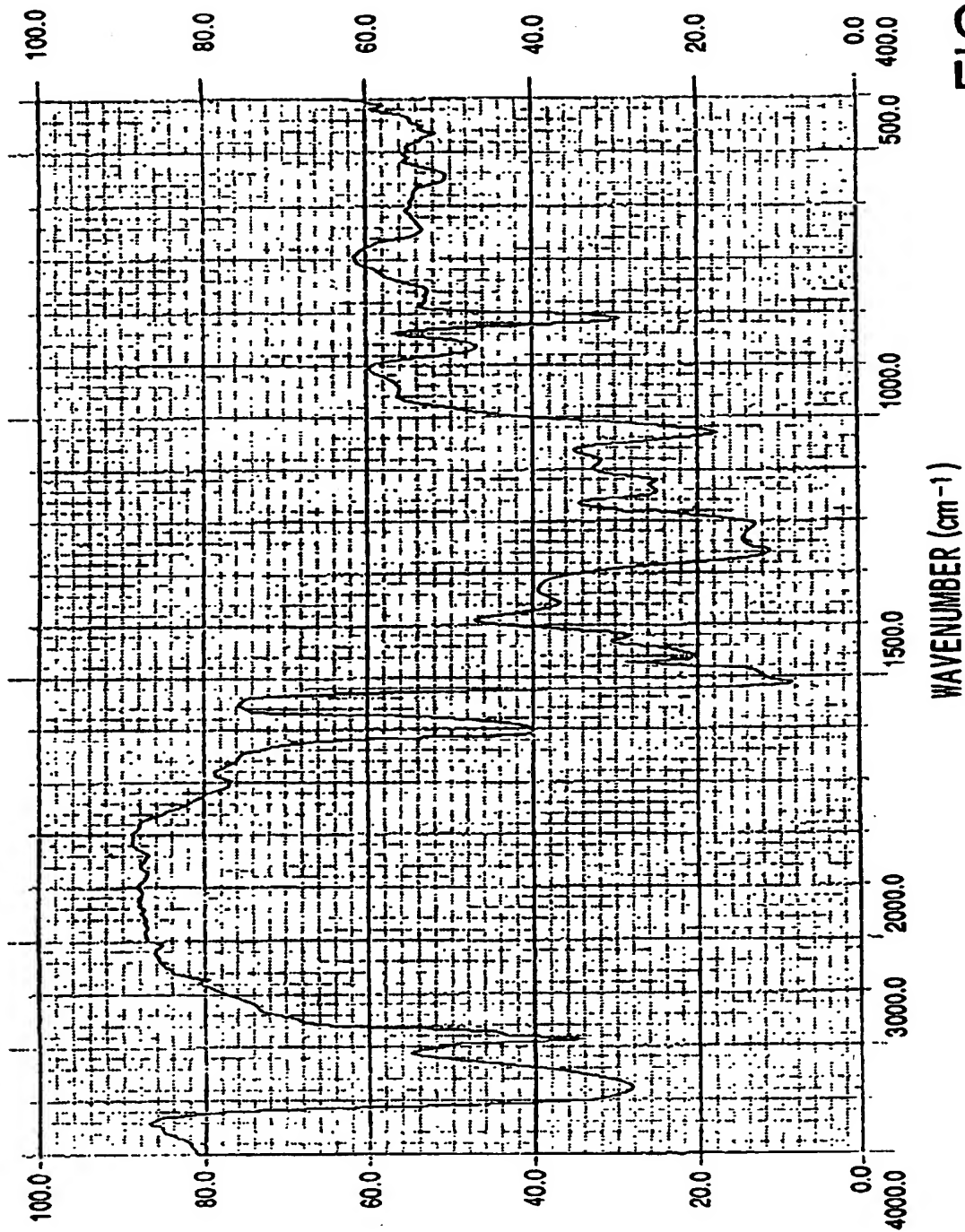


FIG.20

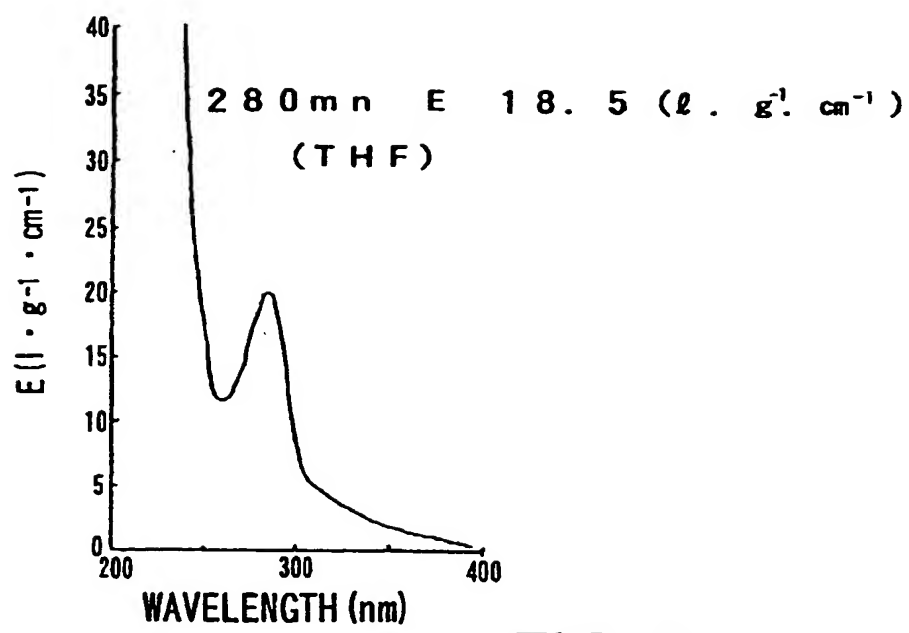


FIG.21

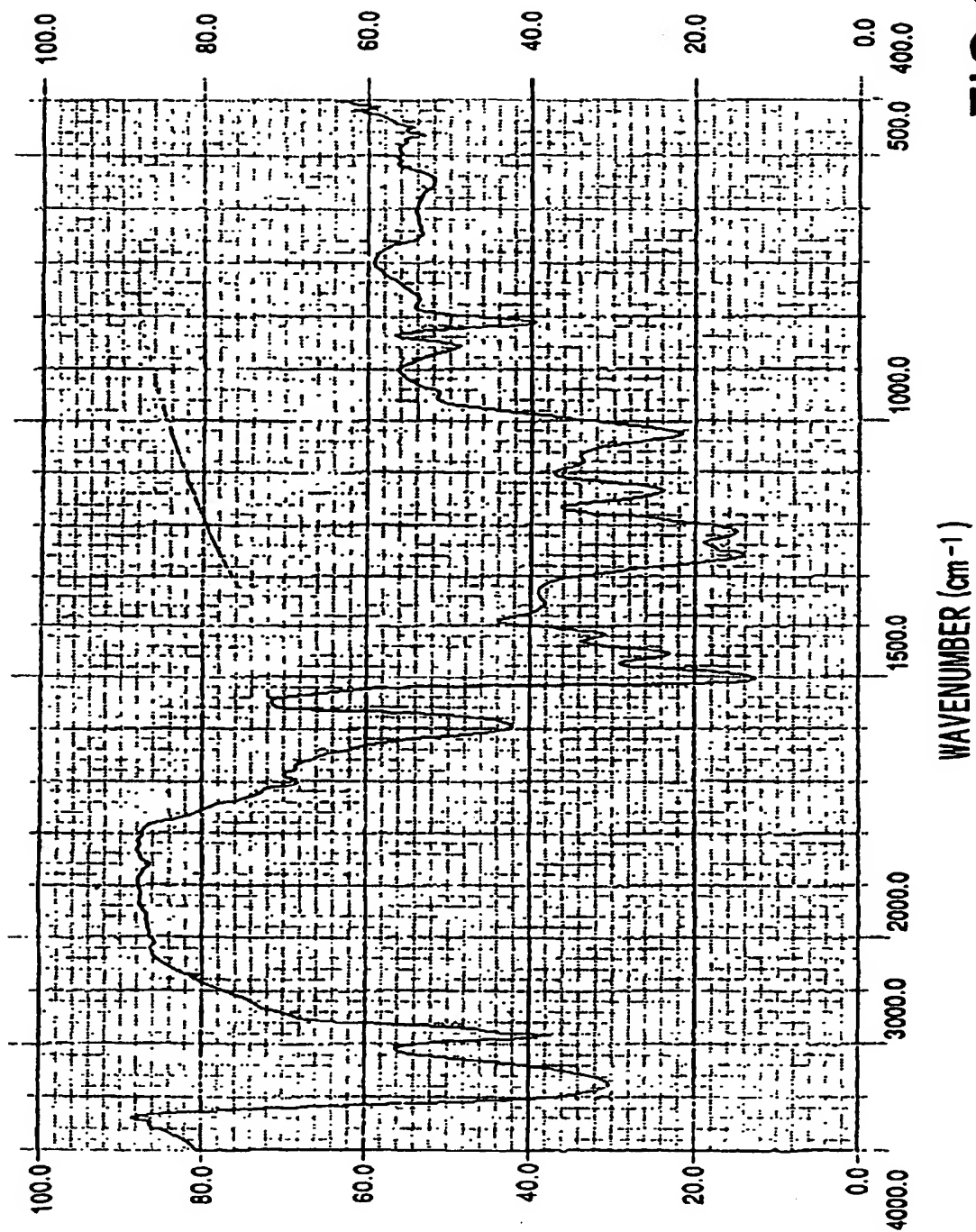
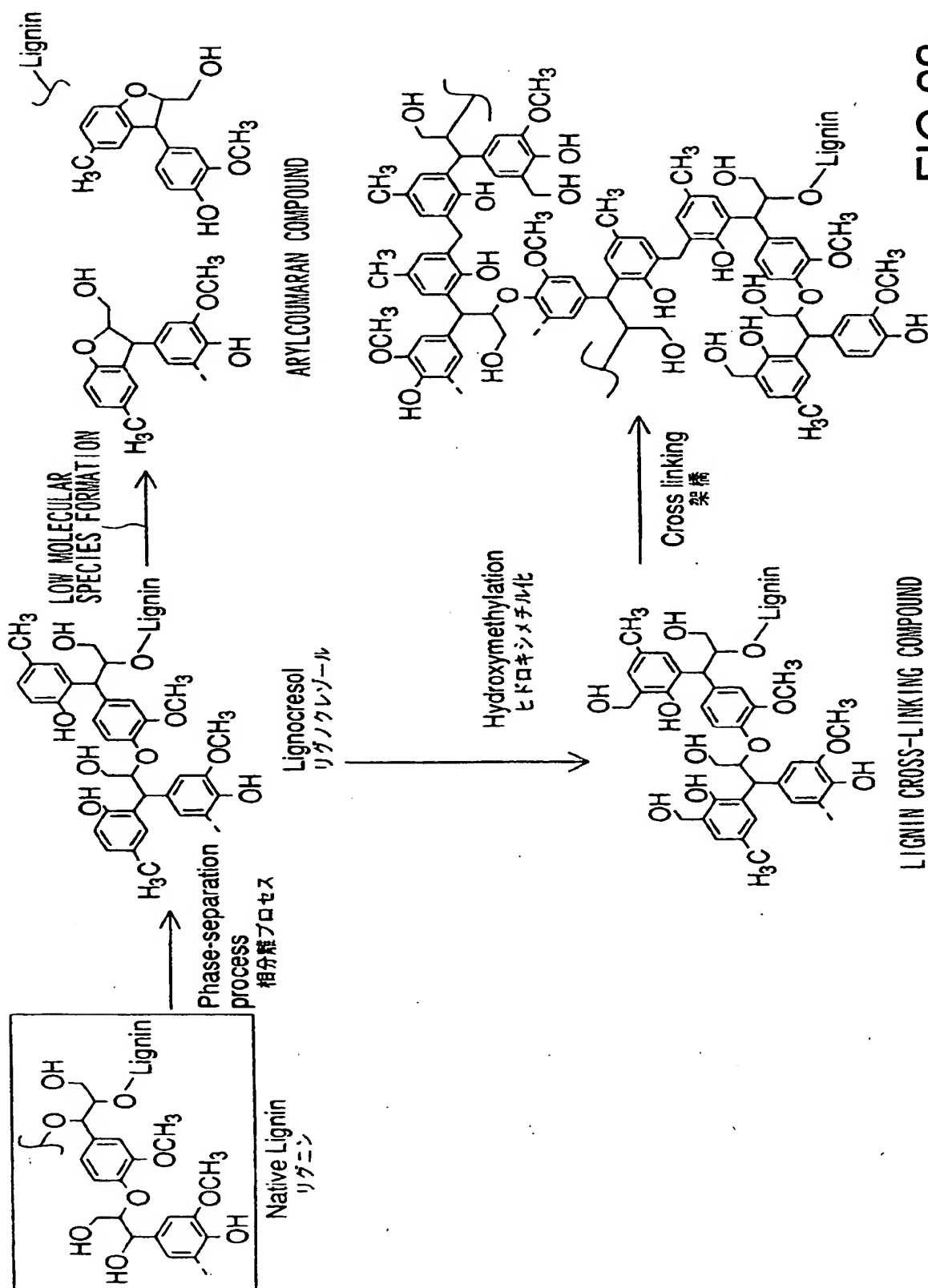


FIG.22



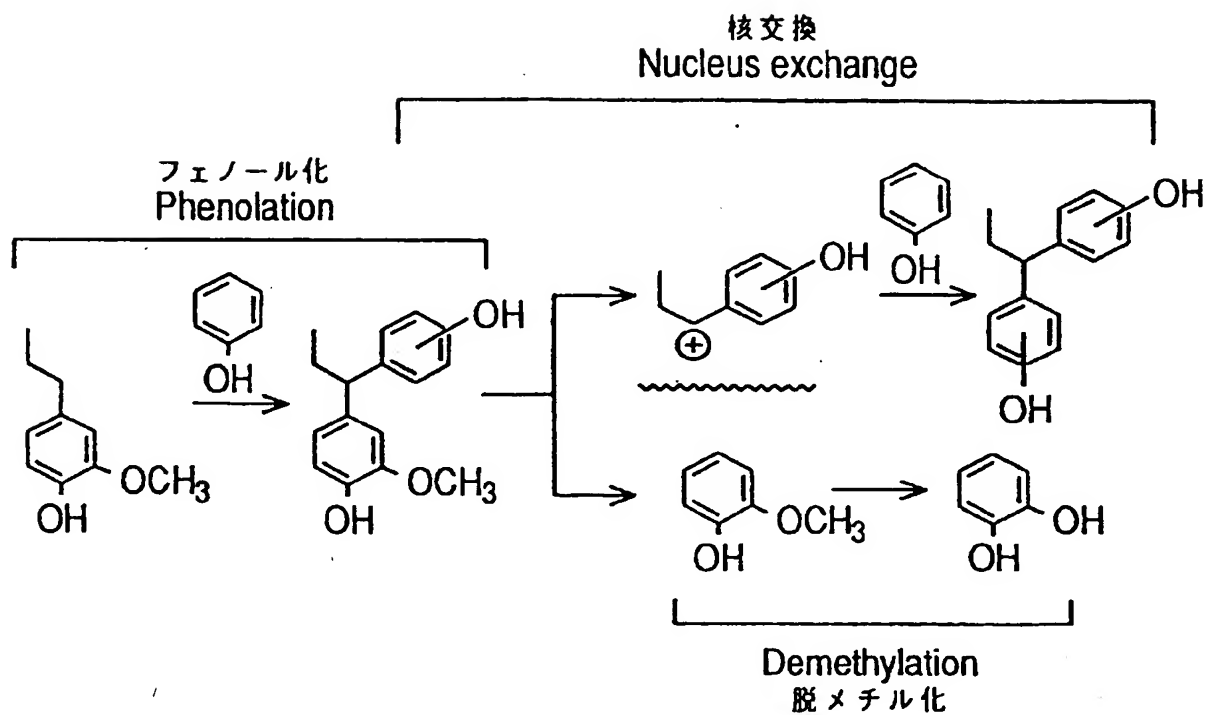


FIG.24

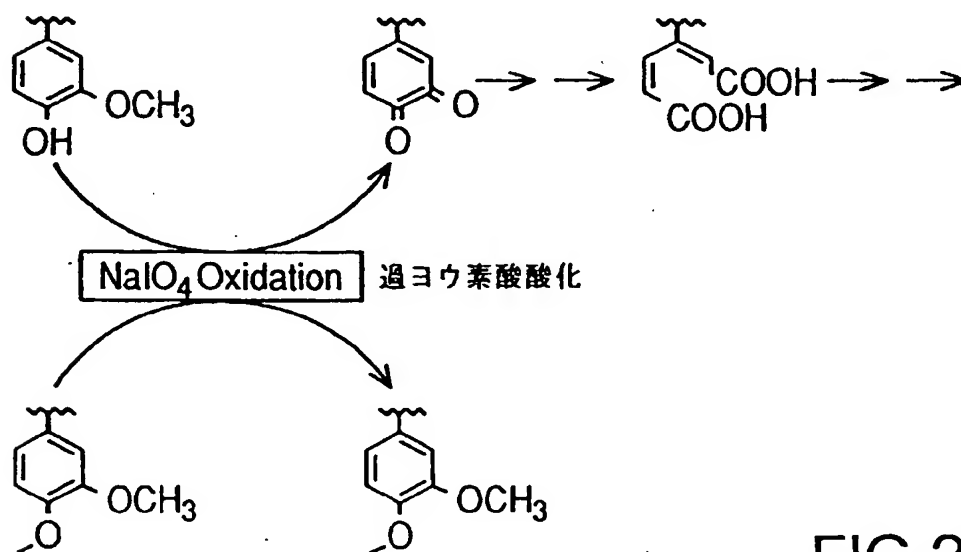


FIG.25

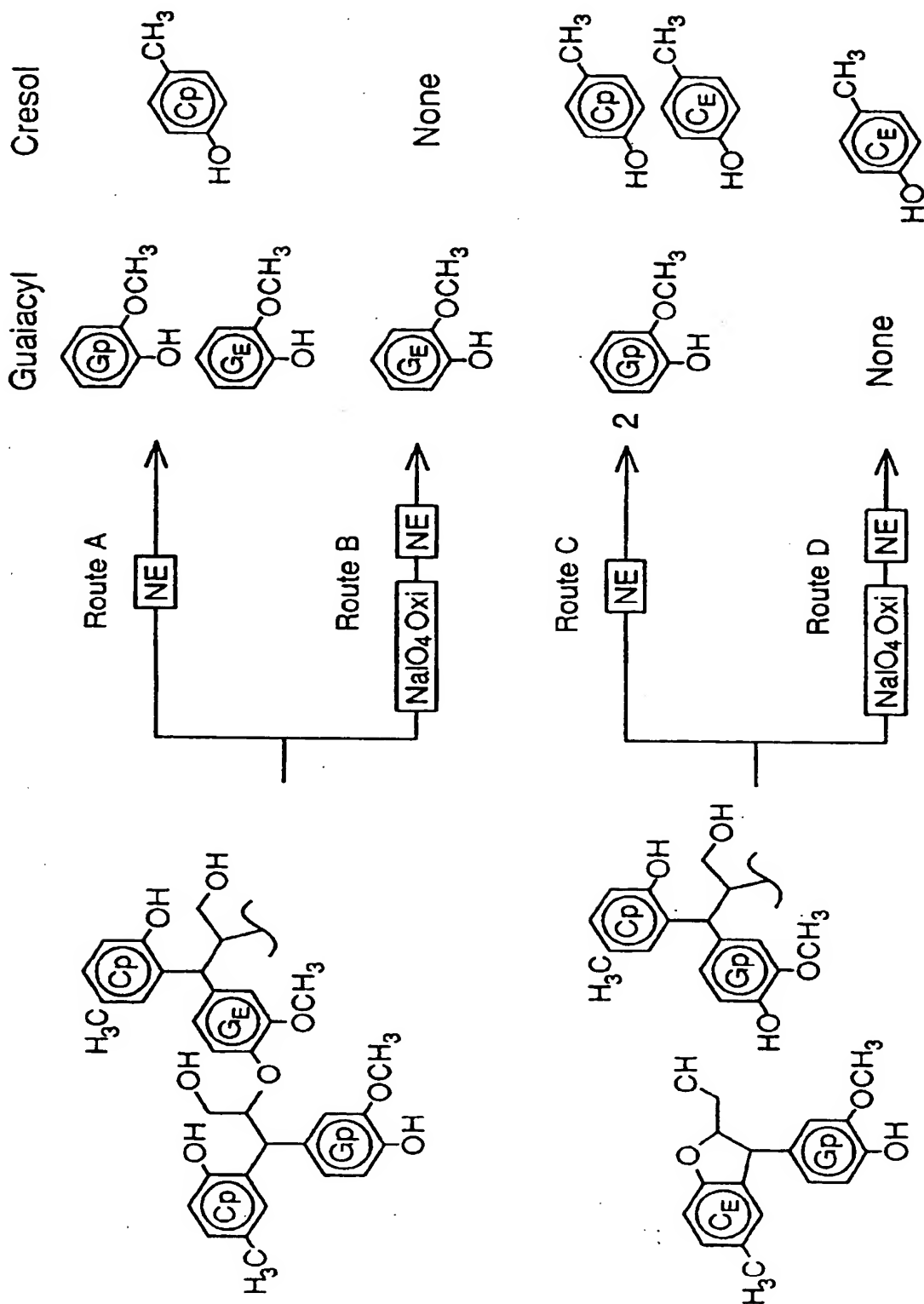


FIG.26

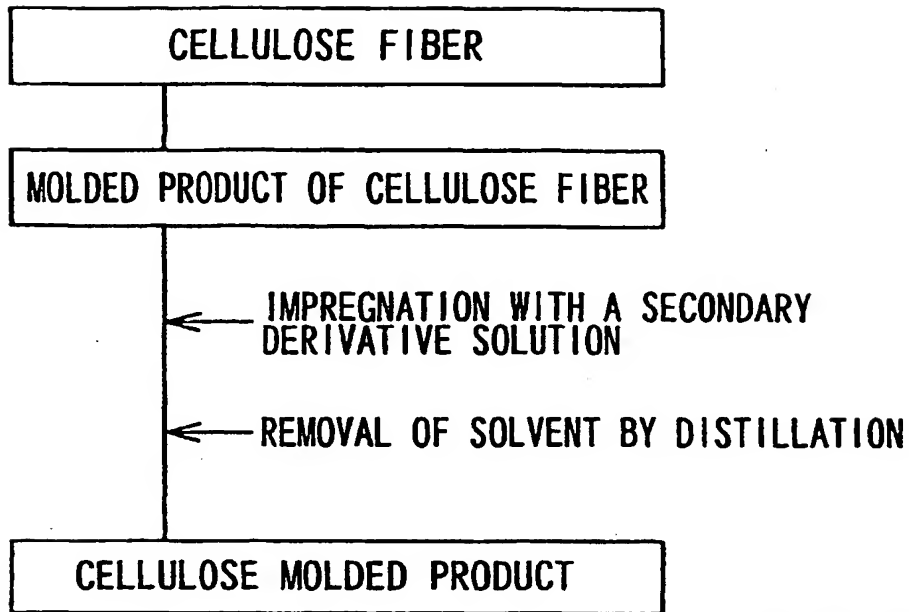


FIG.27

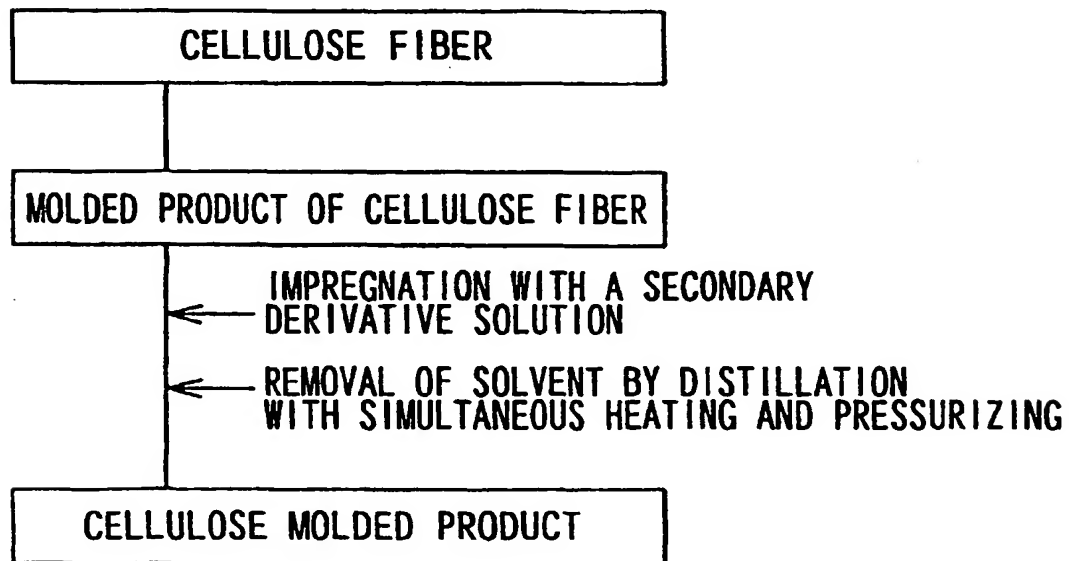


FIG.28

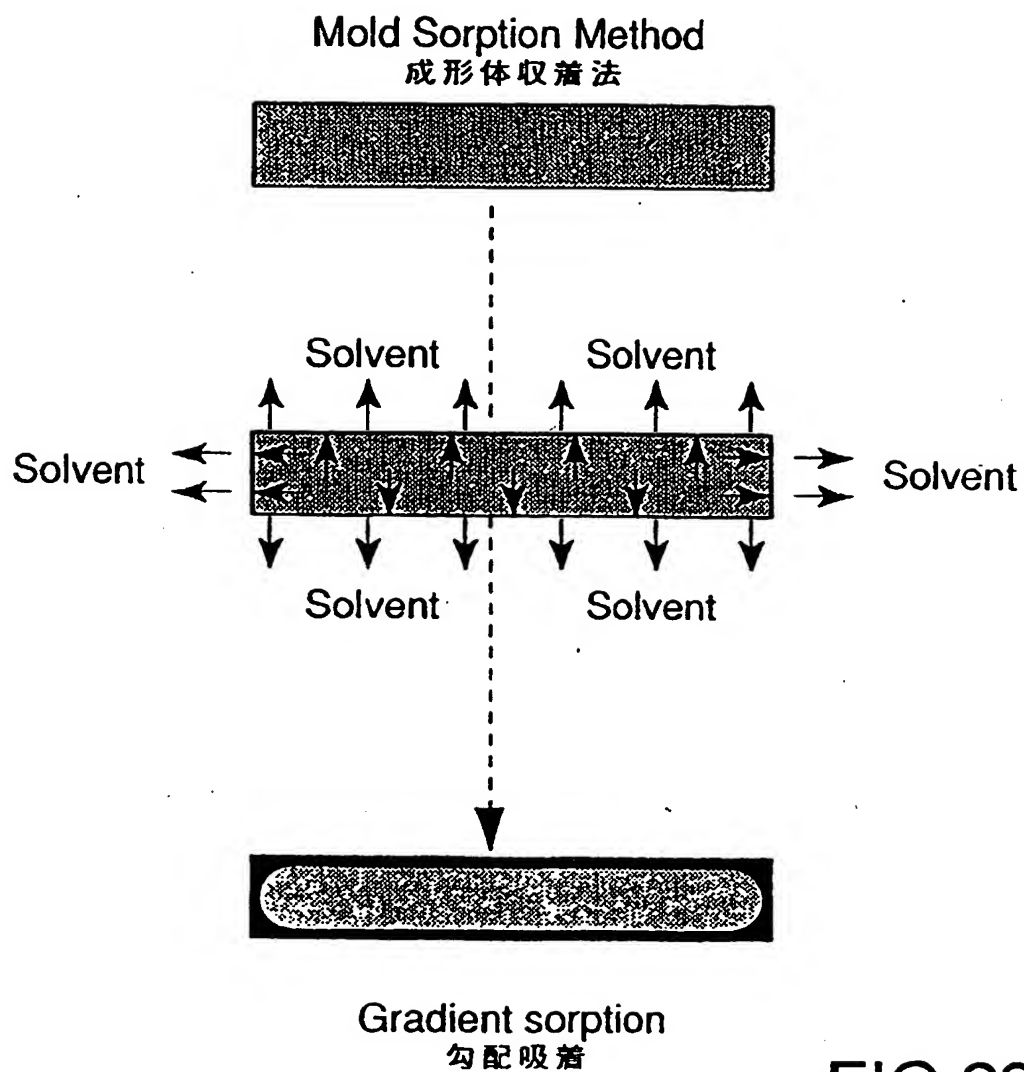


FIG.29

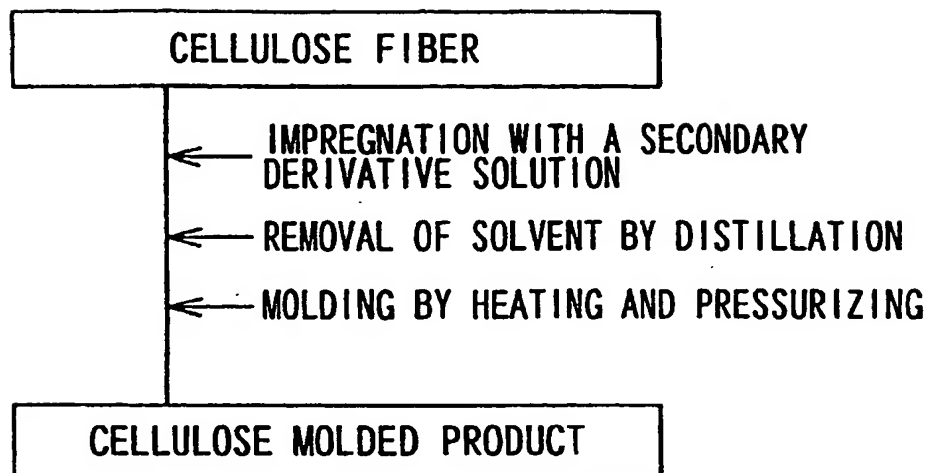


FIG.30

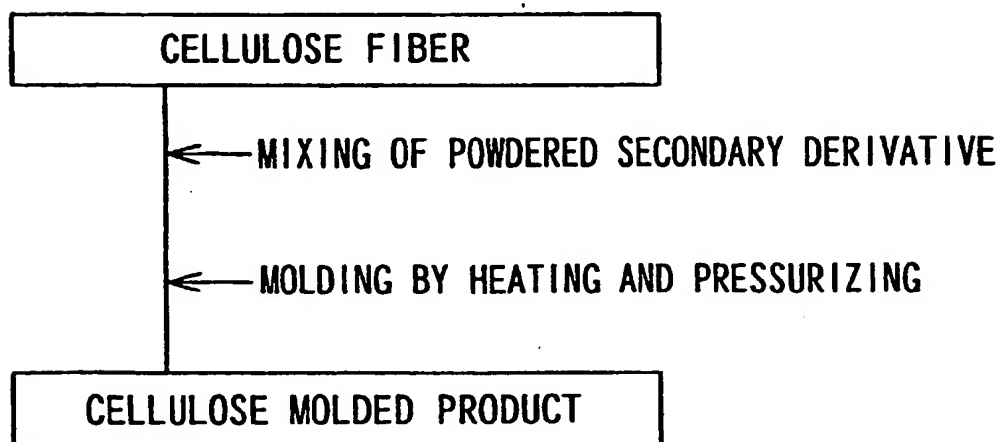


FIG.31

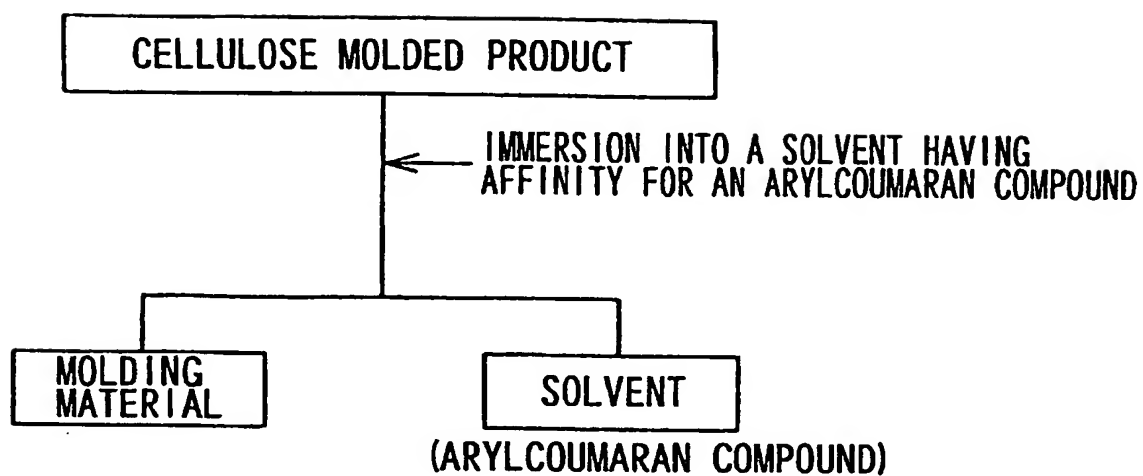


FIG.32

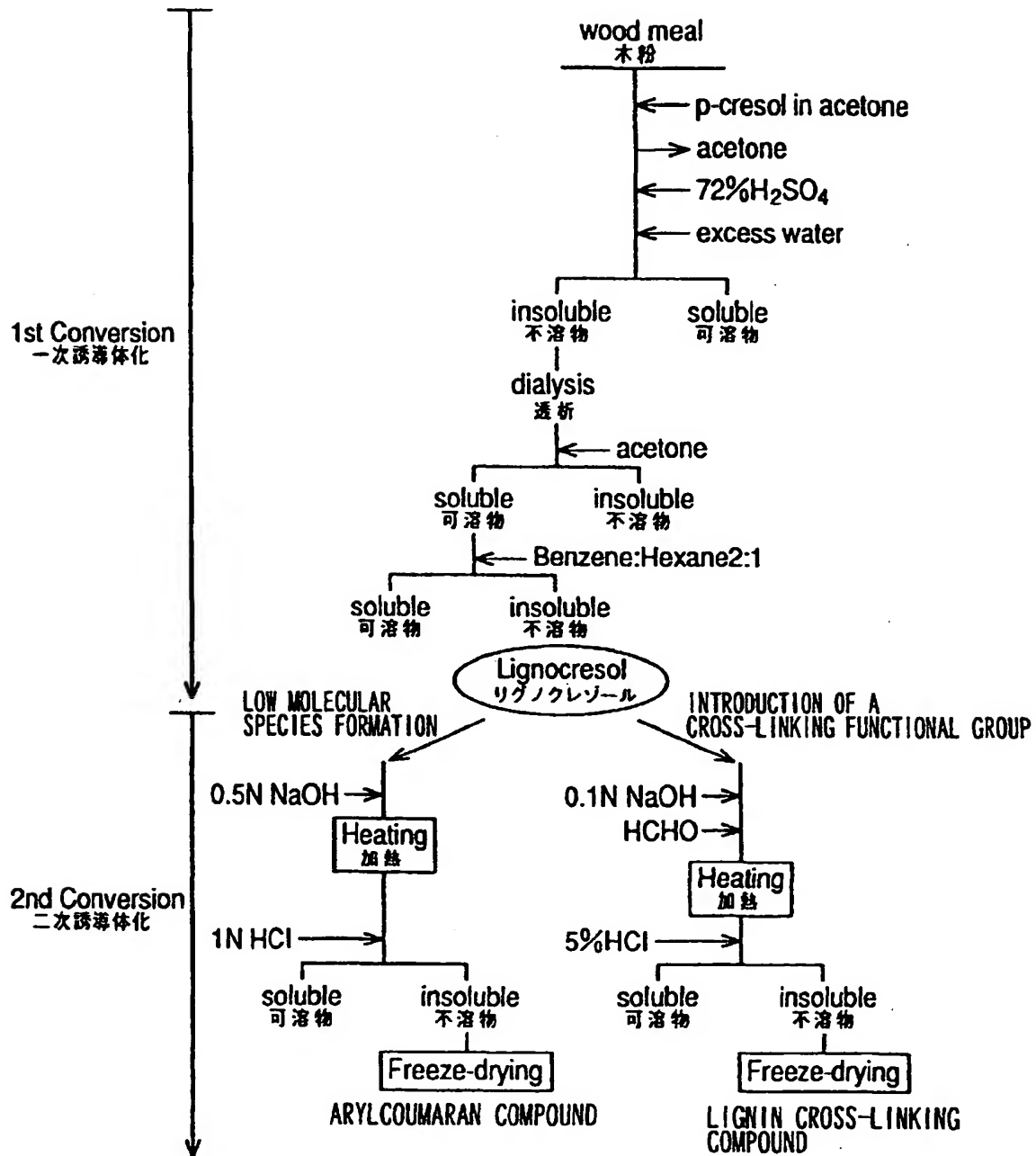


FIG.33

SAMPLE	YIELD (%)	AVERAGE MOLECULAR WEIGHT			AMOUNT OF INTRODUCED CRESOL	
		\bar{M}_w	\bar{M}_n	\bar{M}_w / \bar{M}_n	Wt%	mol/C ₉
LIGNOCRESOL	—	8355	2737	3.053	26.70	0.68
ARYLCOUMARAN COMPOUND	81.07	1261	576	2.190	24.41	0.60

FIG.34

SAMPLE	HYDROXYL GROUP (mol/C ₉)		FREQUENCY OF PHENOLIC RINGS	
	Phenolic Wt% mol/C ₉	Aliphatic Wt% mol/C ₉	Guaiacyl (% of total guaiacyl) (% of total cresol)	Cresol (% of total cresol)
LIGNOCRESOL	9.94	1.60	6.21	1.00
ARYLCOUMARAN COMPOUND	9.75	1.51	7.68	1.19
			46.04	81.14
			67.09	67.83

FIG.35

SAMPLE	YIELD (%)	AVERAGE MOLECULAR WEIGHT			AMOUNT OF INTRODUCED CRESOL	
		\overline{M}_w	\overline{M}_n	$\overline{M}_w / \overline{M}_n$	Wt%	mol/C ₉
LIGNOCRESOL	—	10691	3260	3.279	13.62	0.30
LIGNIN CROSS-LINKING COMPOUND	91.58	2894	919	3.149	13.76	0.30

FIG.36

SAMPLE	HYDROXYL GROUP (mol/C ₉)				HYDROXYMETHYL GROUP (mol/C ₉)	
	Phenolic		Aliphatic			
	Wt%	mol/C ₉	Wt%	mol/C ₉	Wt%	mol/C ₉
LIGNIN CROSS-LINKING COMPOUND	7.75	1.06	10.55	1.44	6.90	0.56

FIG.37

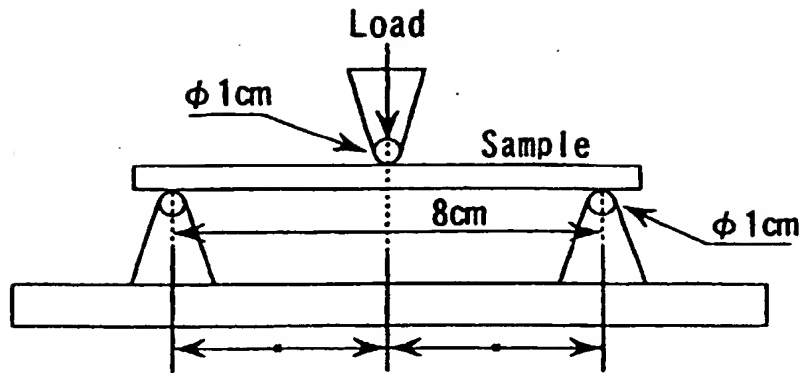
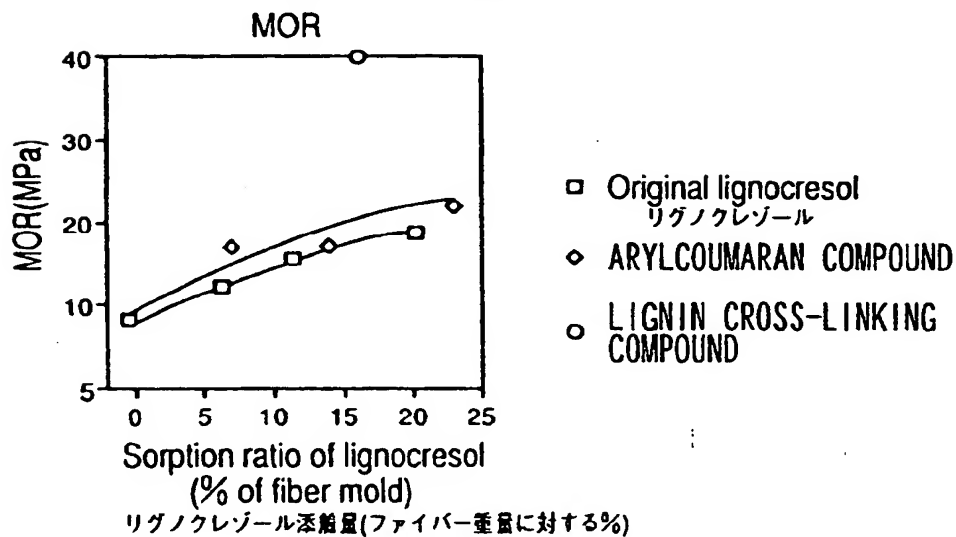
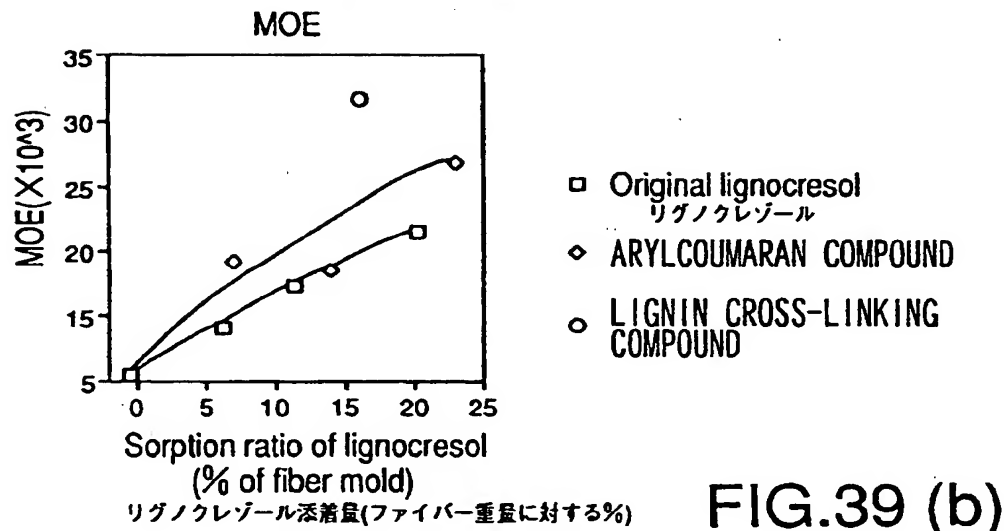
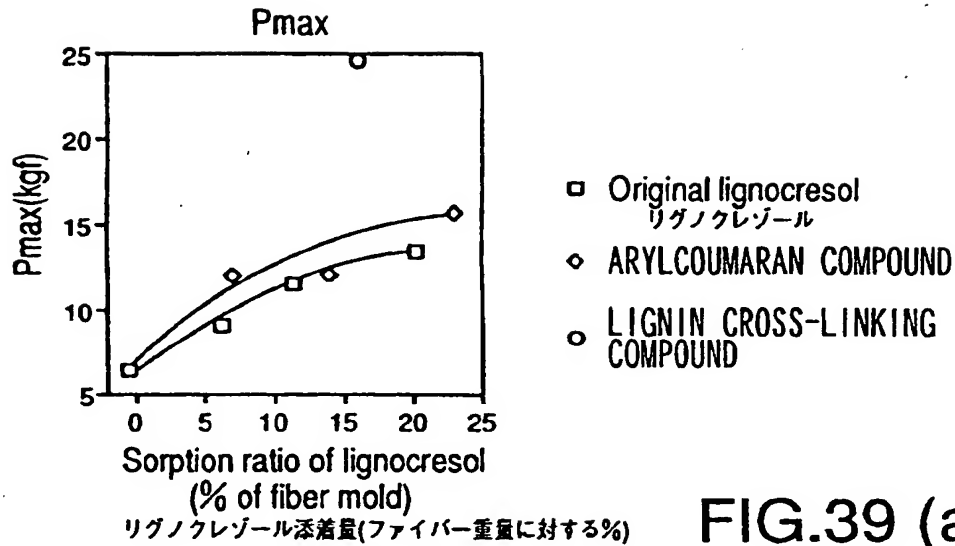
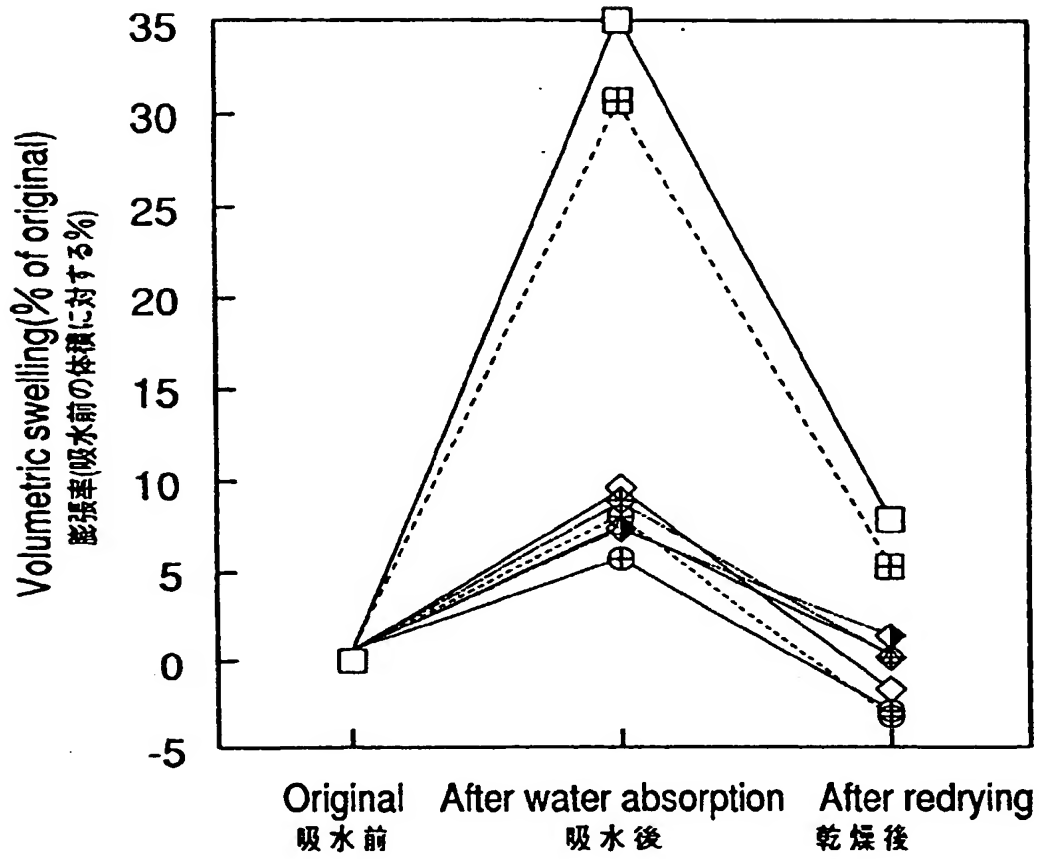


FIG.38





Unheated
加熱処理無

—□—

—◇—

---⊕---

—△—

Control

5%

10%

20%

Heated
加熱処理有

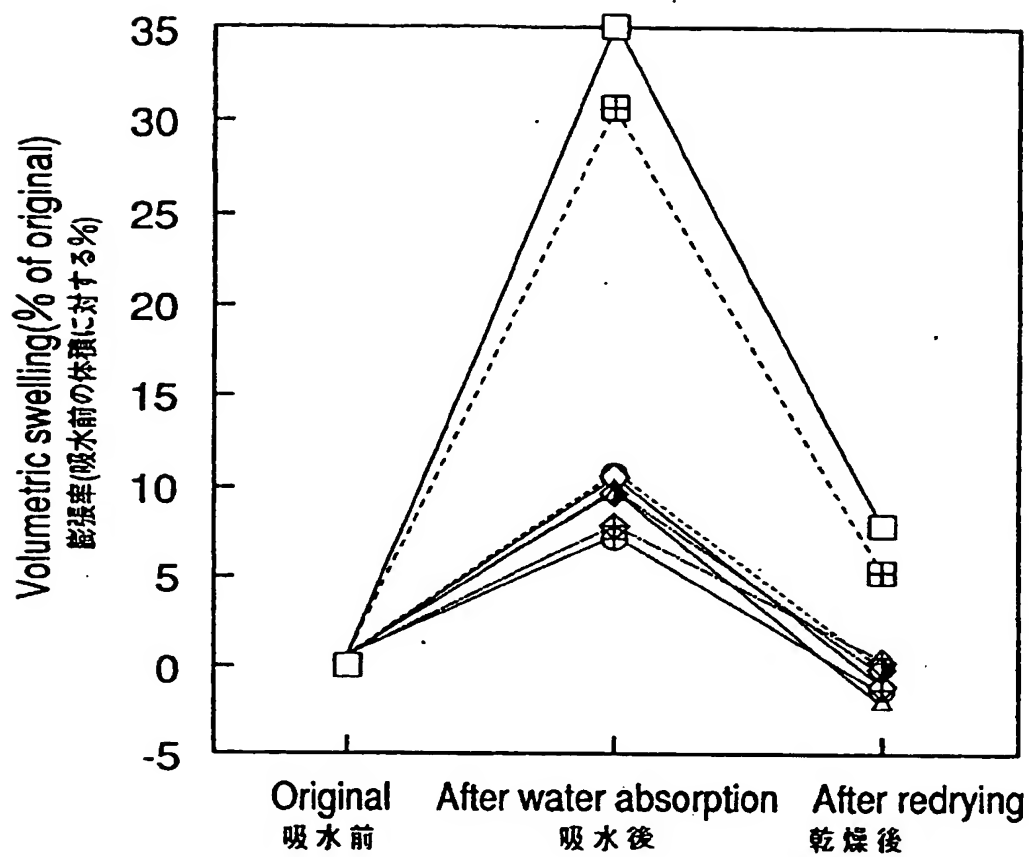
---⊞---

—⊕—

—⊕—

—◆—

FIG.40



Unheated
加熱処理無

—□—

Control

—◇—

5%

---○---

10%

—△—

20%

Heated
加熱処理有

---田---

—◆—

—⊕—

---◆---

FIG.41

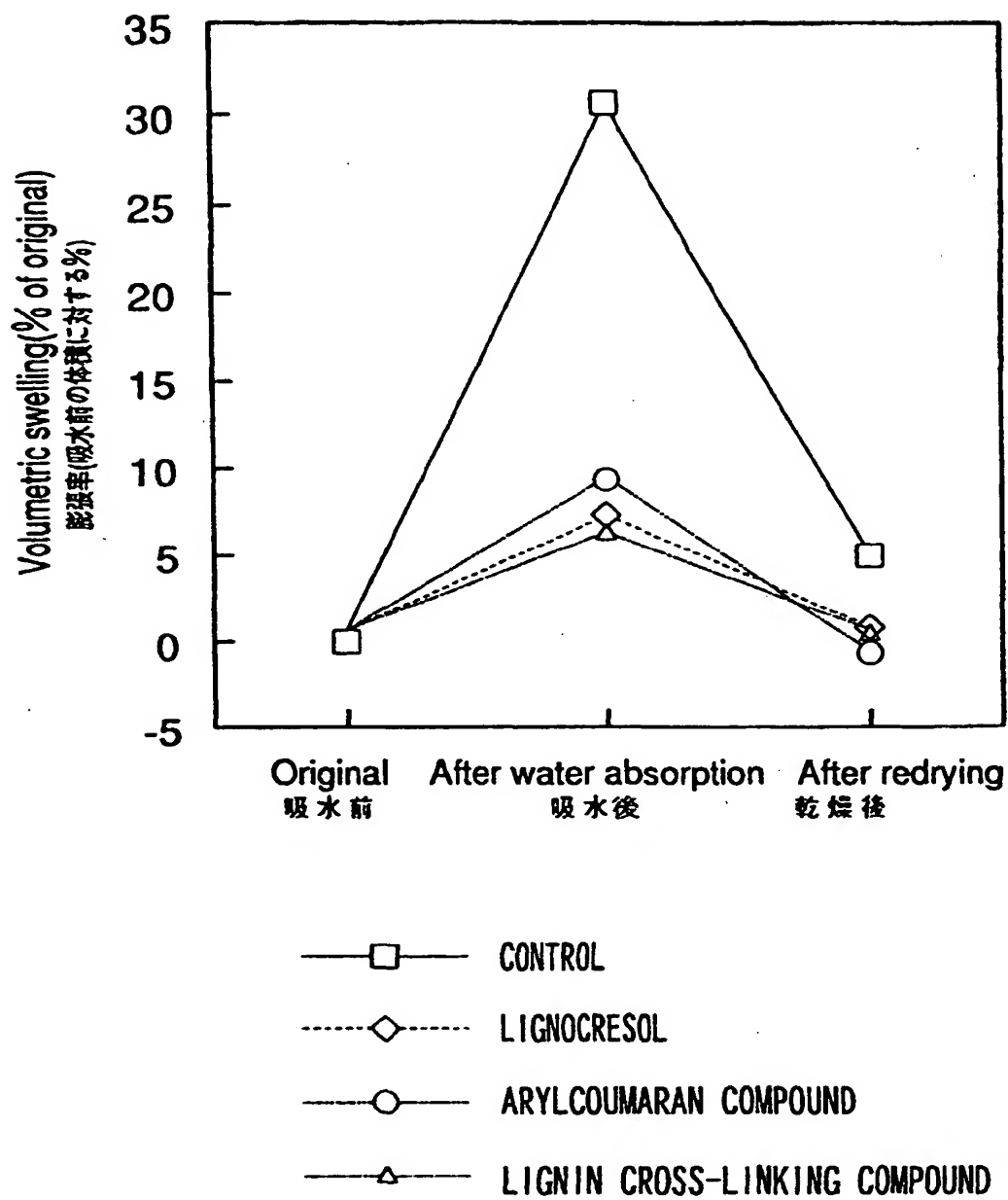


FIG.42

SAMPLE	SPECIFIC GRAVITY	WATER ABSORPTION * 1	VOLUMETRIC INCREASE * 2	
			AFTER WATER ABSORPTION	AFTER DRYING
CONTROL	0.475	167.88	30.52	5.22
LIGNOCRESOL	0.557	15.69	7.43	1.01
ARYLCOUMARAN COMPOUND	0.559	15.64	9.36	-0.51
LIGNIN CROSS-LINKING COMPOUND	0.596	9.34	6.55	0.77

* 1 : % RELATIVE TO WEIGHT BEFORE WATER ABSORPTION

* 2 : % RELATIVE TO VOLUME BEFORE WATER ABSORPTION

FIG.43

**RECOVERY RATE OF A LIGNIN DERIVATIVE FROM A MOLDED PRODUCT
(% RELATIVE TO WEIGHT OF AN ATTACHED LIGNIN DERIVATIVE)**

SAMPLE	UNHEATED	HEATED
LIGNOCRESOL	99.28	94.10
ARYLCOUMARAN COMPOUND	100.00	100.00
LIGNIN CROSS-LINKING COMPOUND	—	Trace

FIG.44

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/03240

A. CLASSIFICATION OF SUBJECT MATTER Int. Cl ⁶ C07G1/00, C08J5/04, C08J7/02 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int. Cl ⁶ C07G1/00, C08J5/04, C08J7/02 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) CAS ONLINE		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP, 2-233701, A (Masamitsu Funaoka), September 17, 1990 (17. 09. 90) (Family: none)	1 - 7
A	JP, 1-16840, A (Westvaco Corp.), January 20, 1989 (20. 01. 89) & US, 4764597, A & DE, 3820253, A1 & SE, 8802039, A & NO, 8802533, A & FI, 8802839, A & ES, 2009200, A	1 - 7
X	Richard M. EDE et al. "Formic Acid/Peroxyformic Acid Pulping", Holzforschung, (1989) Vol. 43, No. 2, p. 127-129	2
X	Seiichi YASUDA et al. "Chemical Structures of Sulfuric Acid Lignin", Holzforschung, (1987) Vol. 41, No. 1, p. 59-65	2
X	Gosta BRUNOW "On the Acid-catalyzed Alkylation of Lignins", Holzforschung, Vol. 45, No. 1, p. 37-40	2
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search December 3, 1997 (03. 12. 97)		Date of mailing of the international search report December 16, 1997 (16. 12. 97)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.		Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP97/03240

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Josef GIERER et al. "Studies on the Condensation of Lignins in Alkaline Media Part 11", Can. J. Chem., (1977) Vol. 55, No. 4, p. 593-599	2

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